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LIQUID CRYSTALLINE DENDRIMERS

Final Technical Report
by

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The influence of molecular construction of LC dendrimers on their phase behavior and properties have been studied. First to five generations of carbosilane LC dendrimers with 8, 16, 32, 64 and 128 terminal mesogenic groups (cyanobiphenyl, methoxyphenyl benzoate, ethyl lactate derivatives, etc.) have been synthesized.

Investigation of thermal behavior and structure of LC dendrimers reveals smectic mesophases over a wide temperature region. LC dendrimers with terminal ethyl-L-lactate-containing mesogenic groups exhibit a chiral smectic C mesophase possessing ferroelectricity. It was found for the first time that LC dendrimers of fifth generation have two levels of structural organization: smectic-like arrangement of mesogenic groups and supramolecular assembling of LC dendrimers in nanostructures of columnar type.

Hydrodynamic and electrooptical properties of solutions of LC dendrimers synthesized have been studied. The results demonstrate, that hydrodynamic behavior of LC dendrimers is similar to the behavior of solid unpermeable particles, which radius of gyration is proportional to the molar mass to the power of 1/3. At the same time, the chain character of these dendrimers is exhibited in temperature dependence of viscosity and small-scale mechanism of their orientation in the electric field, that reflects their polymeric nature.

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Annotation

The Project develops the new scientific direction associated with synthesis and study of a new family of liquid crystalline (LC) dendrimers with terminal mesogenic groups. It is directed towards the understanding of the nature of the LC state of these exotic systems and the search of their potential applications. The influence of molecular construction of LC dendrimers on their phase behavior and properties was studied. For this purpose first to five generations of carbosilane LC dendrimers with 8, 16, 32, 64 and 128 terminal mesogenic groups (cyanobiphenyl, methoxyphenyl benzoate, ethyl lactate derivatives, etc.) were synthesized using hydrosilylation as a key reaction. Molecular structure and purity of all new compounds were characterized by ^{1}H-NMR spectroscopy and GPC analysis.

Investigation of thermal behavior and structure of LC dendrimers by means of polarizing optical microscopy, differential scanning calorimetry (DSC), small and wide angle X-ray scattering (SAXS and WAXS) methods reveals smectic A and C type mesophases over a wide temperature region. LC dendrimers with terminal ethyl-L-lactate-containing mesogenic groups exhibit a chiral smectic C mesophase possessing ferroelectricity. The highest spontaneous polarization was found to be about 140 nC/cm^2 for the LC dendrimer of first generation and it is reduced with increase of the generation number. It was shown that isotropisation temperature increases with increasing of the generation number, whereas the enthalpy of this phase transition decreases. It was found for the first time that LC dendrimers of fifth generation have two levels of structural organization: smectic-like arrangement of mesogenic groups and supramolecular assembling of LC dendrimers in nanostructures of columnar type. This is the first example of LC dendrimers with terminal calamitic mesogenic groups forming columnar mesophases. Possible structures of all mesophases formed are discussed.

Hydrodynamic and electrooptical properties of solutions of LC dendrimers synthesized were studied by viscosimetry, diffusion and electrooptical birefringence (Kerr effect). The results demonstrate, that hydrodynamic behavior of LC dendrimers is similar to the behavior of solid unpermeable particles, which radius of gyration is proportional to the molar mass to the power of 1/3. At the same time, the chain character of these dendrimers is exhibited in temperature dependence of viscosity and small-scale mechanism of their orientation in the electric field, that reflects their polymeric nature.

List of key words

Liquid Crystals, Dendrimers, Liquid Crystalline Dendrimers, Synthesis, Hydrosilylation, Phase Behavior, Structure, Nanostructure, Columnar Mesophases, Smectics, Kerr Effect, Hydrodynamic properties, Ferroelectrics

Contents

1. Introduction

Since the very beginning of 90th a new field of chemistry and physical chemistry of high molar weight compounds associated with synthesis and study of superbranched oligomers and polymers, called dendrimers, actively develops. The number of branchings in the molecule of dendrimer increases in geometrical progression when increasing the molar mass. It leads to a change of the shape and the rigidity of the molecules and, as a rule, is accompanied by unusual dependences of some properties of dendrimers (such as viscosity, solubility, density, etc) on their molar mass. Main peculiarities of dendrimers, which mainly determine the physical properties and phase behaviour, are their uniform, highly branched structure, narrow polydispersity, large number of terminal groups and lacking of entanglements. Having a different structure of the core and the terminal groups, each dendritic molecule, being a small particle with given mass and dimensions, can be considered as a "unimolecular micelle". These peculiarities of molecular structure of dendrimers predetermine a number of distinguishing features of their physico-chemical properties such as high solubility, low viscosity, low glass transition temperatures as well as capacity to act as dendritic boxes, i. e. to encapsulate molecules.

Liquid crystalline (LC) dendrimers containing terminal mesogenic groups are an essential interest among different dendrimers due to their unusual molecular construction combining structural units capable for LC mesophase formation (mesogenic groups) together with dendritic (regularly super-branched) topology. Each molecule of such LC dendrimer can be presented schematically as a sphere, the internal part of which consists of non-mesogenic blocks, while the external one consists of mesogenic fragments:
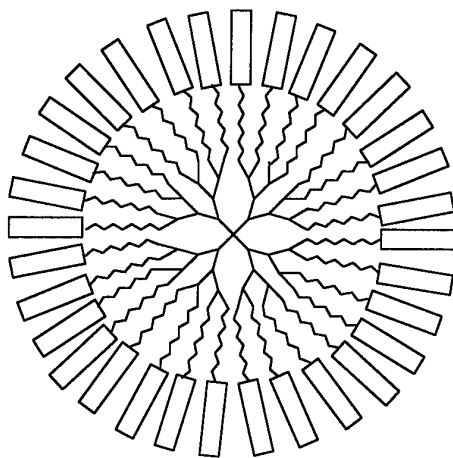
Such "microheterogenic" structure of molecules of LC dendrimers should predetermine a tendency of such system to microphase separation like it happens for block- and graft- copolymers, which often form different mesomorphic structures of lamellar, hexagonal and other types. Bearing in mind the above-mentioned, the study of the structural organization of the dendrimers constructed from dissimilar blocks, part of which is capable to form LC mesophase, undoubtedly, presents substantive scientific interest from structural point of view.

Possibility of "LC jacket" creation around the central core formed by the dendritic matrix, fairly, is interesting from the practical point of view also, because it opens up prospects for use such compounds, for example, as modificators of mechanical, rheological and tribological properties of polymers, as well as for creation on their base some selective membranes and drug delivery systems.

The main goal of the work was to perform the systematic investigation of LC dendrimers as a new class of LC high molar mass compounds in order to understand the nature of the LC state of these exotic systems and find some ways for their potential applications. For this purpose a number of carbosilane LC dendrimers with different molecular structure have been synthesized and studied. Correlation between molecular structure of carbosilane LC dendrimers and their physico-chemical behaviour in bulk and dilute solutions has been determined.

2. Synthesis of carbosilane LC dendrimers

The general approach to the synthesis of carbosilane LC dendrimers is described below. The key moment here is coupling of the mesogenic groups to the active terminal groups of the dendritic matrices, therefore special attention was devoted to the choose of appropriate chemical reaction. This reaction should satisfy a number of complex requrements permitting to produce pure final compounds with a high yield. By the authors viewpoint, the hydrosilylation reaction is one of the best satisfying these criteria.

Taking into account the similarity of structure of the compounds in question and comb-shaped LC polymers, as well as dependencies known for such polymers, mesogenic groups were linked to the dendritic matrices not directly, but through the long aliphatic spacers. The elaborated approach to the synthesis of carbosilane LC dendrimers consists of the following main steps:

1) divergent synthesis of carbosilane dendritic matrices of different generations with terminal allyl groups;

2) synthesis of mesogenic precursors containing aliphatic spacer and the terminal active Si-H group;

3) coupling of the mesogenic precursors synthesized to the carbosilane dendritic matrices.

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2.1. Synthesis of carbosilane dendritic matrices

G-1(Cl)8   G-1(Allyl)8

G-2(Cl)16   G-2(Allyl)16

G-3(Cl)32   G-3(Allyl)32

$\xrightarrow{i}$ G-4(Cl)64 $\xrightarrow{j}$ G-4(Allyl)64 $\xrightarrow{i}$ G-5(Cl)128 $\xrightarrow{j}$ G-5(Allyl)128
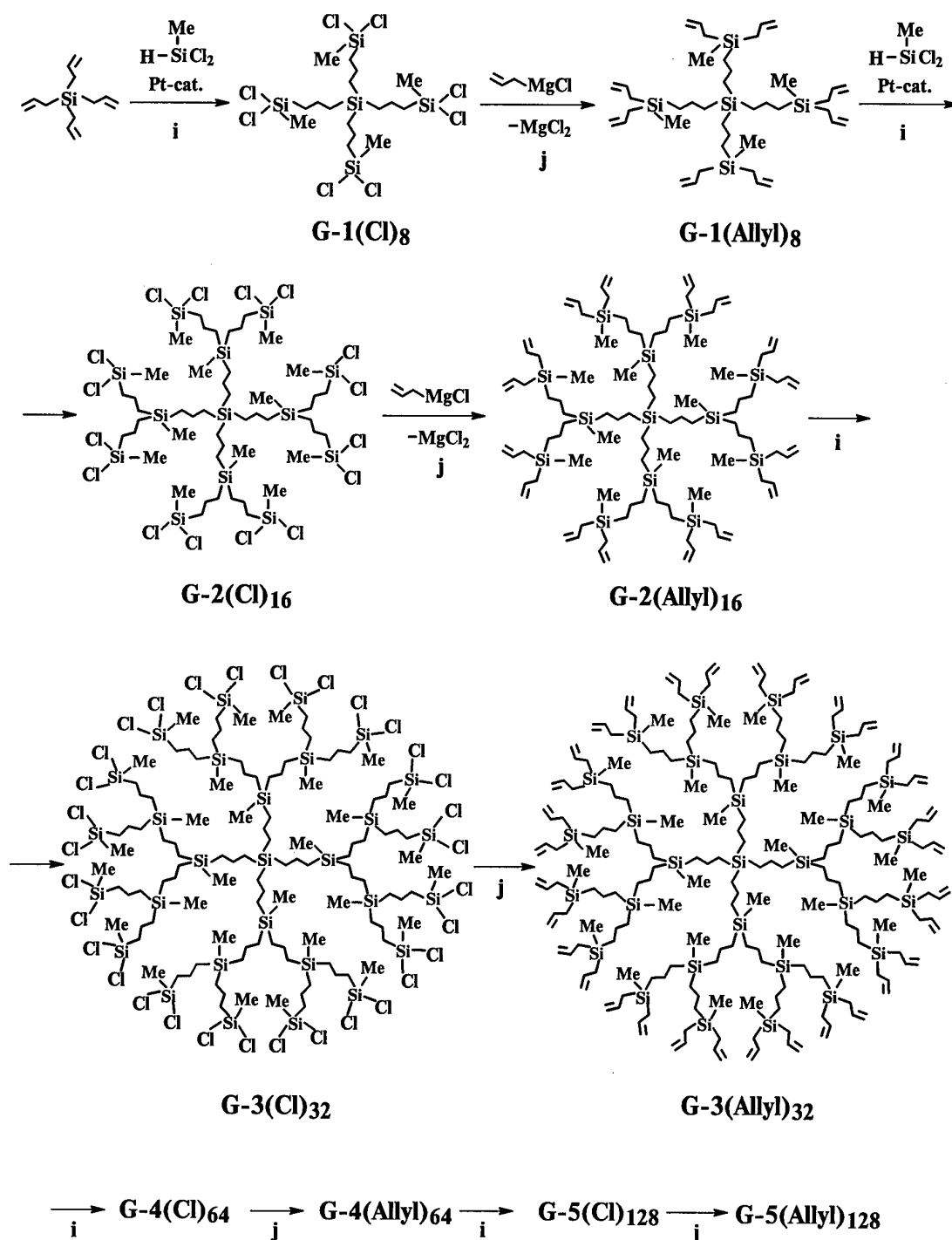
Figure 1. Scheme of synthesis of the initial carbosilane dendrimers with terminal allyl groups.

Synthesis of initial carbosilane dendrimers with the terminal allyl groups *G-n(All)ₘ* was carried out according to the scheme shown in Fig.1.[i] Detailed description of the synthesis has been published in the paper [1]. Some features of carbosilane dendrimers synthesized should be noted here. As can be seen from the Fig.1, these dendrimers were produced by a divergent approach via a Grignard/hydrosilylation reiterative stepwise technique. They have four-functional central branching core and three-functional branching units leading to the degree of branching on the each step equal to two. That differs them from carbosilane dendrimers described in the literature before. Five generations of the carbosilane dendritic matrices containing 8, 16, 32, 64 and 128 terminal allyl groups for the generations 1, 2, 3, 4, and 5 respectively have been synthesized (see Fig.1) in order to determine a correlation between the number of generation of LC dendrimers and their phase behaviour.

The structure of all carbosilane dendrimers synthesized was confirmed by ^{1}H-NMR spectroscopy (see Attachment 1). Purity and individuality of these compounds was confirmed by GPC analysis (see Attachments 2, 3). As can be seen from these data, all carbosilane dendrimers synthesized are monodisperse substances with polydispersity less then 1.01. High purity of these dendrimers was achieved by the method of preparative HPLC.

2.2. Synthesis of mesogen-containing precursors

Synthesis of mesogenic precursors containing aliphatic spacer and the terminal active Si-H group capable of reacting with the terminal allyl groups of carbosilane dendritic matrices was performed according to the schemes shown in Figures 2 and 3. They differ from each other by the way of linking of the mesogenic groups to the aliphatic spacers. In the case of undecylenic spacer (Fig. 2) ester link was used, while in the case of penthylene spacer (Fig. 3) ether link was used. The choice of the synthetic scheme was dictated by the accessibility of the reagents.

In order to trace the influence of the chemical nature of mesogenic groups on the phase behaviour of LC dendrimers two different mesogenic precursors were synthesized according to the scheme presented in Fig. 2: with cyanobiphenyl **(CB)** (a) [1] and methoxyphenyl benzoate **(MPhB)** (b) [2] mesogenic groups.

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[i] In the formula *G-n(X)ₘ* : *n* is generation number; *m* is the number of terminal groups *X* shown in the parenthesis.

Mes–OH + Cl–C(=O)~~~~ $\xrightarrow[-N(Et)_3 \cdot HCl]{N(Et)_3}$ **Mes**–O–C(=O)~~~~ $\xrightarrow[Pt\text{-cat.}]{HSi(Me)_2Cl}$

$\longrightarrow$ **Mes**–O–C(=O)~~~~$Si(Me)_2$–Cl $\xrightarrow[-Py \cdot HCl]{H_2O;\,HSi(Me)_2Cl;\,Py}$ **Mes**–O–C(=O)~~~~$Si(Me)_2$–O–$Si(Me)_2$–H

where **Mes** =
a) N≡C–⬡–⬡– (CB)

b) CH₃O–⬡–OOC–⬡– (MPhB)
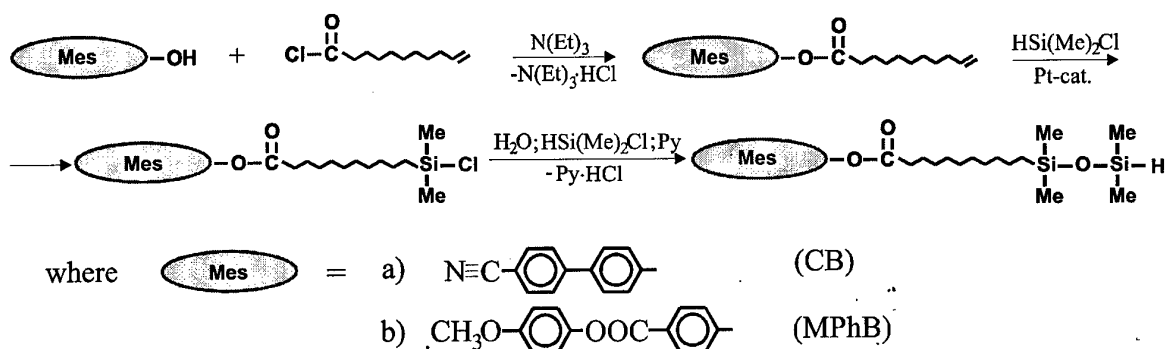
Figure 2. Synthesis of mesogenic precursors with undecylenic ($-(CH_2)_{10}CO-$) spacer **H-Si-Und-Mes**.

For evaluation of the influence of the spacer length on the phase behaviour of LC dendrimers, along with the mesogenic precursor containing cyanobiphenyl mesogenic group and undecylenic spacer **(Und)** described above the precursor containing cyanobiphenyl mesogenic group and pentylenic spacer **(Pent)** was synthesized according to the scheme presented in Fig. 3.
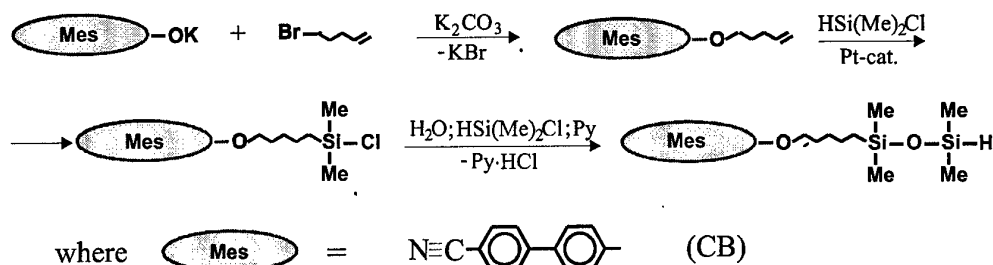
Mes–OK + Br~~~ $\xrightarrow[-KBr]{K_2CO_3}$ **Mes**–O~~~ $\xrightarrow[Pt\text{-cat.}]{HSi(Me)_2Cl}$

$\longrightarrow$ **Mes**–O~~~$Si(Me)_2$–Cl $\xrightarrow[-Py \cdot HCl]{H_2O;\,HSi(Me)_2Cl;\,Py}$ **Mes**–O~~~$Si(Me)_2$–O–$Si(Me)_2$–H

where **Mes** = N≡C–⬡–⬡– (CB)

Figure 3. Synthesis of the mesogenic precursor with penthylenic ($-(CH_2)_5-$) spacer **H-Si-Pent-CB**.

In other words, the synthesis of all the mesogenic precursors includes receiving of double bond containing mesogenic compounds, then hydrosilylation of them with dimethylchlorosilane to produce Si-Cl terminal group in the mesogenic precursors and finally cohydrolysis of them with 40-fold excess of dimethylchlorosilane to yield desirable Si-H terminal group. Purification of all mesogenic precursors synthesized was achieved by means of column chromatography on silica gel.

The purity and the structure of all novel compounds synthesized were approved by the methods of NMR ^{1}H spectroscopy (see an example in the Attachment 1) and thin layer chromatography.

Special attention was given to the synthesis of chiral mesogenic precursors, possessing chiral smectic C mesophase responsible for ferroelectric properties (see section 2.2.1).

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2.2.1. Synthesis of chiral mesogenic precursors.

In order to produce LC dendrimers showing ferroelectric properties, multi-step synthesis of special chiral mesogenic precursors possessing chiral smectic C mesophase has been carried out. Derivatives of ethyl-L-lactate have been chosen for this purpose due to their accessibility and high values of the spontaneous polarization P_s. Main steps of the synthesis of such chiral monomer with terminal carbon-carbon double bond (**Und-PBL**) are schematically shown in Figure 4 [3, 4].
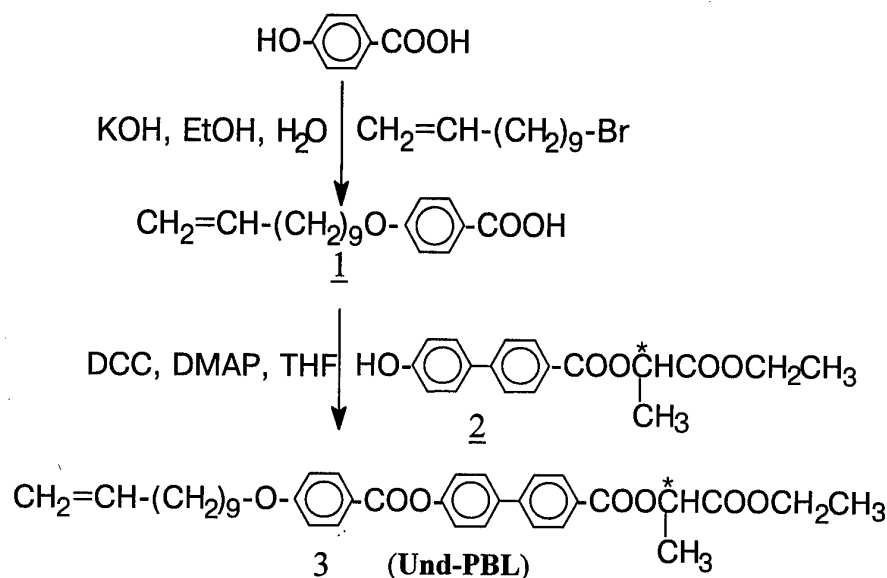

Figure 4. Scheme of synthesis of ferroelectric vinyl monomer (**Und-PBL**).

Etherification reaction of 11-bromo-1-undecene with 4-hydroxybenzoic acid gave 4-(11-undecenoyloxy)-benzoic acid (**1**). Chiral biphenolic ester **2** was synthesised by coupling ethyl-L-lactate with 4-methoxycarbonyloxy-biphenyl-4-carboxylic acid under standard conditions and subsequent deprotection with ammonia in ethanol. The mesogenic α-olefin **3** was prepared by etherification of **1** with the compound **2** and purified by silica gel column chromatography. The chemical structure of the compound **3** (L)-(+)-4-[1-(ethoxycarbonyl)-(ethoxy-carbonyl)] biphenyl-4'-(10-undecenyl-oxy)phenyl-4'-carboxylate (**Und-PBL**) has been confirmed by ^{1}H NMR spectroscopy (see Attachment 1).

The ferroelectric vinyl monomer **Und-PBL** received was involved in the following hydrosilylation and cohydrolysis reactions like it was shown in Figure 2 to give ferroelectric mesogenic silane **H-Si-Und-PBL** capable for production of chiral LC dendrimers (see section 3.3).

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2.3. Synthesis and purification of LC dendrimers

Coupling of the mesogenic precursors to the dendritic matrices was carried out by the hydrosilylation reaction under the presence of Pt catalysis (Fig. 5).
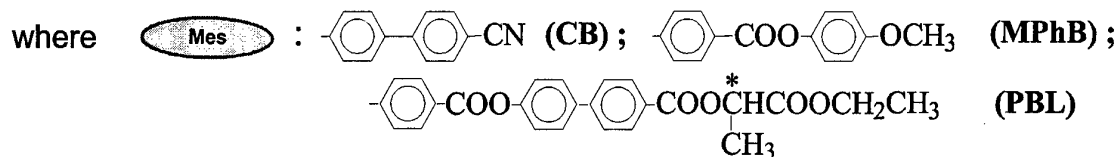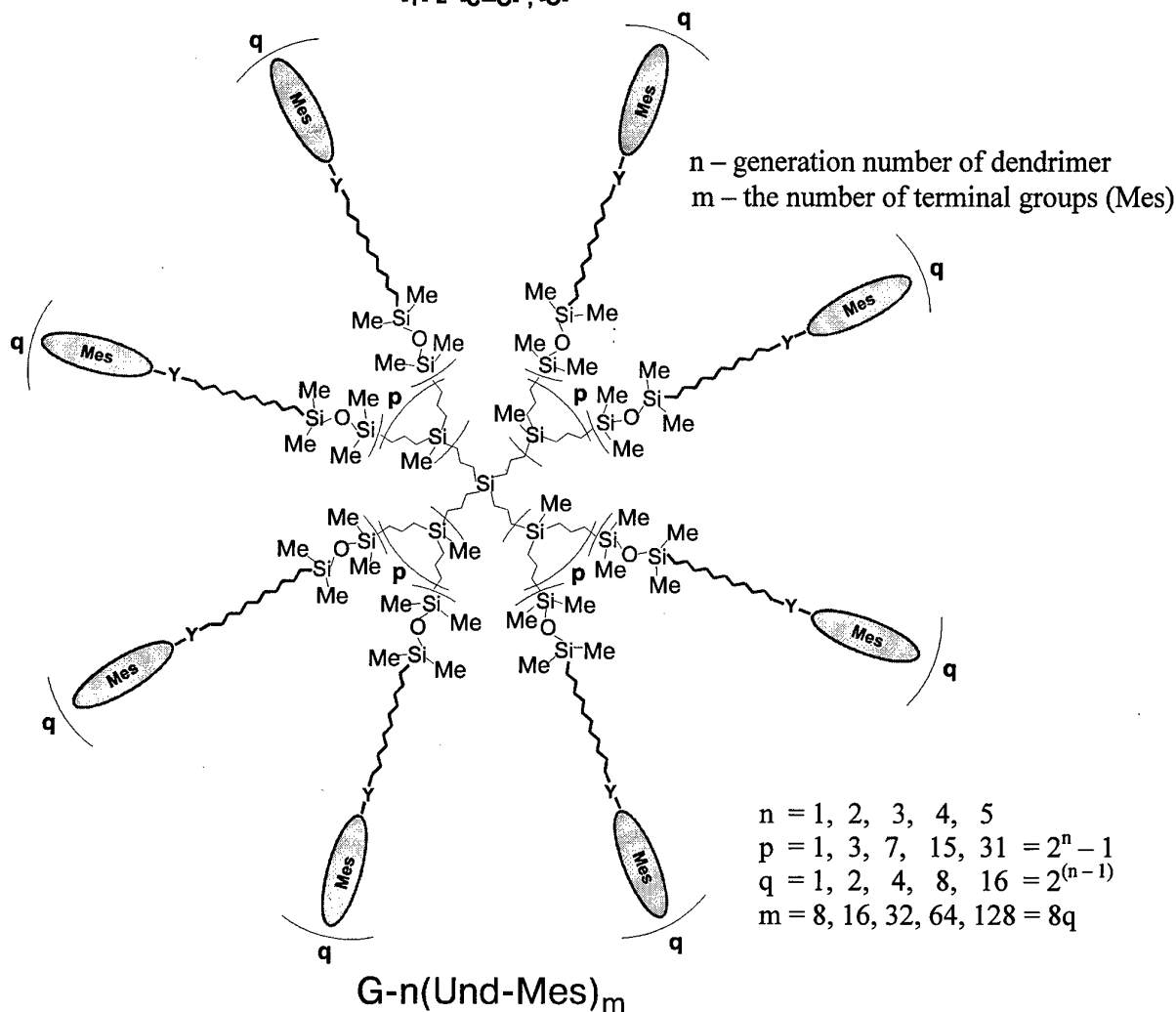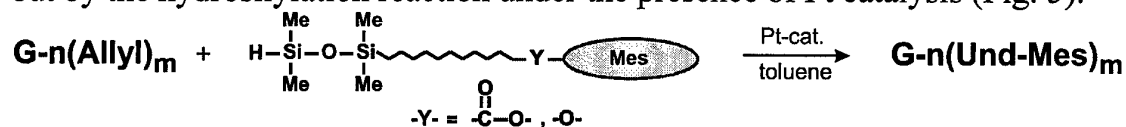

n – generation number of dendrimer
m – the number of terminal groups (Mes)

$n = 1, 2, 3, 4, 5$
$p = 1, 3, 7, 15, 31 = 2^n - 1$
$q = 1, 2, 4, 8, 16 = 2^{(n-1)}$
$m = 8, 16, 32, 64, 128 = 8q$

Figure 5. Synthesis and general structural formulae of LC dendrimers
G-n(Und-Mes)$_m$

The reactions were carried out in solutions of the initial reagents in a toluene. For all the cases 1.5 to 2.0-fold excess of the mesogenic silane was used in order to guarantee a complete coupling of the mesogenic groups to all terminal allyl groups of the dendritic matrices. Reactions were continued until the compete disappearance of the allyl double bonds signals in the NMR ^{1}H spectra.

After completion of the reaction the excess of the mesogenic silane was removed by the column chromatography with silica gel for LC dendrimers of generations 1 ÷ 3 and by the boiling with methanol for LC dendrimers of generations 3 ÷ 5. Final purification of the LC dendrimers was conducted by the method of preparative GPC or fractionating by methanol/ethanol from the solution in benzene/toluene.

Individuality and purity of all the LC dendrimers synthesized were approved by the methods of NMR ^{1}H spectroscopy (see Attachment 1) and GPC (see Attachments 2 and 3). Narrow monodisperse peak corresponds to each of the LC dendrimers, which confirm the individuality of the compounds obtained. It is clearly seen from the data adduced that under increase of the generation number of LC dendrimers the molar mass determined using the polystyrene standards deviate more and more from to theoretically calculated molar mass (Attachment 3). The same deviation was observed for the initial dendritic matrices with the allyl terminal groups. These results indicate that under increase of the generation number the density of the LC dendritic molecules increase too, which leads to decrease of a hydrodynamic radius of them in comparison with the molecules of linear polystyrene. It is worth to remind, that dendrimers have lower hydrodynamic volume than their linear analogs due to compact molecular architecture of the former. The data of NMR ^{1}H spectroscopy also indicate the increase of packing density of the mesogenic groups in a surface layer of LC dendritic molecules: observable shift of the signals of the mesogenic group and the spacer protons to the stronger field takes place under increase of the generation number.

In order to evaluate the influence of the spacer length of the phase behavior of LC dendrimers the dendrimer of forth generation with cyanobiphenyl groups and aliphatic spacer containing 5 methylenic groups **G-4(Pent-CB)$_{64}$** was produced. Synthesis of this compounds was completely the same as described above. Molecular mass characteristics of this dendrimer are also presented in the Attachment 3.

3. Study of phase behavior, molecular and supramolecular structure in bulk

Now let us consider the influence of the different structural constituents of LC dendritic molecules on their phase behavior and structure of mesophases

formed. The influence of the generation number is regarded for two homologues series of LC dendrimers: with cyanobiphenyl [5] and methoxyphenyl benzoate [2] mesogenic groups. Comparison of them also allows to find out correlation between the chemical nature of the terminal mesogenic groups and the types of mesophases formed by LC dendrimers [6, 7]. The influence of the spacer length is traced for LC dendrimers with cyanobiphenyl mesogenic groups with different spacers. Properties of ferroelectric LC dendrimers will be considered in a separate chapter.

Phase diagrams for the series of LC dendrimers **G-n(Und-CB)$_m$** and **G-n(Und-MPhB)$_m$**, where n – the generation numbers, m – the number of terminal mesogenic groups, are shown in Fig. 6. As is seen from the data presented, LC dendrimers of the generations $1 \div 4$ form disordered smectic A and C type mesophases only, while LC dendrimers of the generation 5 form additional supramolecular columnar mesophases D_{rec} and D_{hd}. Types of the mesophases were determined by the data of X-ray measurements (small and wide angle X-ray scattering - SAXS and WAXS), differential scanning calorimetry (DSC) and polarizing optical microscopy. Let us consider firstly the phase behaviour and the structure of LC dendrimers lower generations.

3.1. LC dendrimers forming lamellar structures only

DSC curves of all LC dendrimers from the series **G-n(Und-CB)$_m$** are characterized by the second order phase transitions at $T = -20 \div -22\,^{\circ}C$, corresponding to the glass transition temperature T_g, as well as the first order phase transitions at $T = 90 \div 110\,^{\circ}C$, corresponding to the transition from LC mesophase to isotropic melt (see Attachment 4).

The first order phase transitions appear also at the region of $50 \div 60\,^{\circ}C$ for LC dendrimers of the generations $1 \div 3$ (slightly depending on the generation number) (Fig. 6a). Polarizing optical microscopy data showed that fan-shaped texture characteristic of SmA mesophase is seen below this phase transition. Broken fan-shaped texture characteristic of SmC mesophase is seen above the transition. Small and wide angle X-ray scattering confirmed the existence of SmA mesophase for all the dendrimers under consideration: one diffuse peak corresponding to disordered arrangement of mesogenic groups in the layers presents at wide angles as well as two sharp peaks corresponding to 1st and 2nd order reflections from the smectic layers are seen at small angles of the X-ray patterns [8, 9]. However, the data of X-ray measurement did not shown any strong confirmation of the existence of the tilted SmC mesophase. At the temperature region of SmA – SmC phase transition there was not found neither considerable change of the tilt angle of mesogenic groups nor notable changes of interlayer

distances, that is, possible, explained by a disordering of pre-oriented samples during the experiment, because they have low T_g. However, these data do not rule out the possibility of the existence of SmC mesophase with the low tilt angle of mesogenic groups in relation to the smectic layers (less then $10°$). Nevertheless, juxtaposition of DSC, polarizing optical microscopy and X-ray data indicate the existence of SmC mesophase for LC dendrimers of the generations $1 \div 3$.
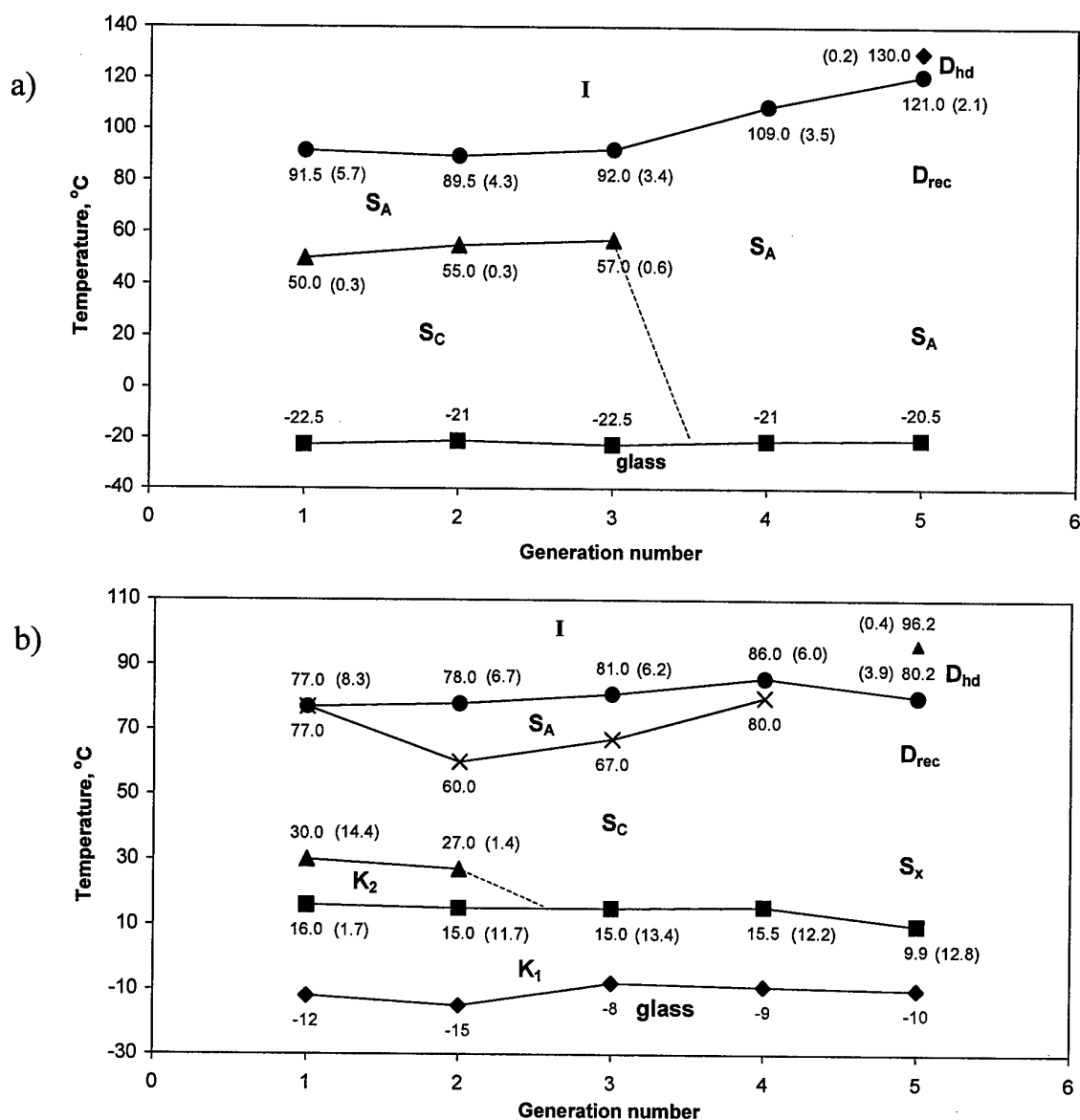
a)

b)

Figure 6. Phase diagrams for series of LC dendrimers **G-n(Und-CB)$_m$** (a) and **G-n(Und-MPhB)$_m$** (b). Enthalpies of the transitions are shown in the parenthesis in J/g.

It is seen from the data presented that in general for both series of LC dendrimers the temperature of the transition SmA - I increases but the enthalpy (and entropy) decreases under increasing of the generation number. Temperature of the transition SmC – SmA increases also under increasing of the generation number for both series of LC dendrimers, although it looks stronger for **G-n(Und-MPhB)$_m$**.

It should be noted that the glass transition temperatures lie below 0 °C and do not depend of the generation number for given series of LC dendrimers but do depend on the type of the terminal mesogenic groups. Some additional low temperature crystalline structures are formed in the case of LC dendrimers with methoxyphenyl benzoate mesogenic groups. However, SmA and SmC mesophases are formed in both cases.

Let us compare now the structures of both series of LC dendrimers, and then consider the structural polymorphism of LC dendrimers of fifth generations, for example, for LC dendrimer **G-5(Und-CB)$_{128}$** .

The dependence of the interlayer distance **d** on the generation number at the same temperature (40 °C) for all the LC dendrimers in question is shown on Fig. 7.
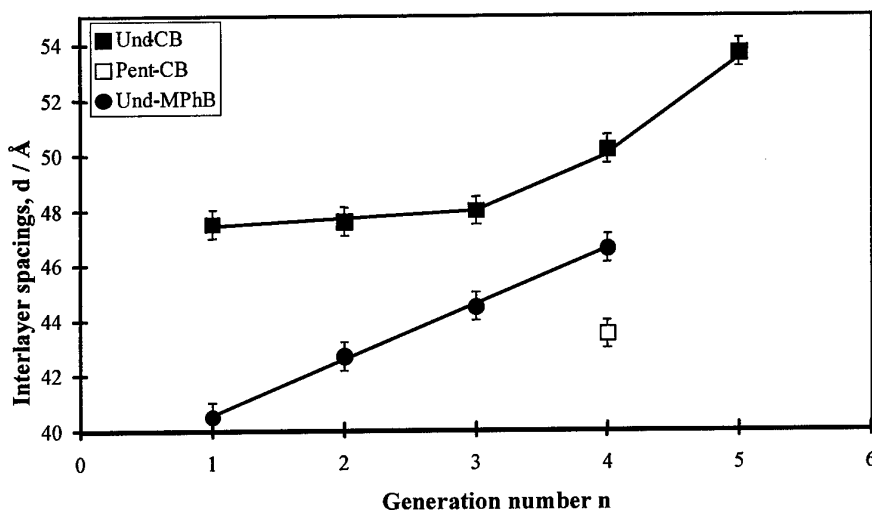

Figure 7. The dependence of the interlayer distance **d** on the generation number for LC dendrimers at the same temperature (40 °C).

It is seen from the data presented that the value of **d** is always lower for **G-n(Und-MPhB)$_m$** then for **G-n(Und-CB)$_m$** in the case of the same generation number of LC dendrimers. It means that a degree of overlapping of methoxyphenyl benzoate mesogenic groups in the smectic layer is higher then that of cyanobiphenyl mesogenic groups. Besides, the dependence of **d** on the generation number is linear for the series of LC dendrimers **G-n(Und-MPhB)$_m$** , while the

values of **d** slightly change for lower generations of **G-n(Und-CB)$_m$**, but they greatly increase starting from the fourth generation. Analysis of these results allowed to suggest the following schemes of packing of mesogenic groups in the smectic layers for both series of LC dendrimers (Fig. 8).
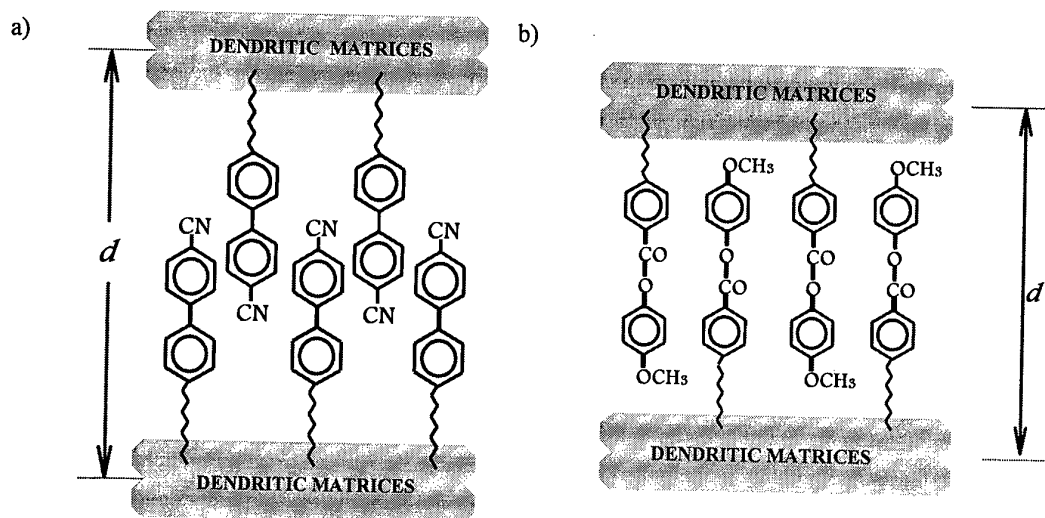

Figure 8. Scheme of packing of the mesogenic groups in the smectic layer: with partial overlapping of the side groups for **G-n(Und-CB)$_m$** (a) and with full overlapping of the side groups for **G-n(Und-MPhB)$_m$** (b).

Cyanobiphenyl containing dendrimers form one layered packing with the partial overlapping of mesogenic groups in the layers (Fig. 8a) due to interactions between strong CN-dipoles and easy polarized benzene rings. Such type of the packing is typical for low-molar-mass alkoxycyanobiphenyls. Moreover, the interlayer distance does not actually change for the first - third generations of **G-n(Und-CB)$_m$**. Thus, a degree of this overlapping should increase with increasing of the generation number. Starting from generation 3 the values of **d** increase that indicates that the degree of this overlapping became constant.

In the case of methoxyphenyl benzoate containing dendrimers, which do not contain large dipoles, one layered packing with full overlapping of the mesogenic groups is realized only (Fig. 8b).

Thus, the main feature of both types of packing is determined by a microsegregation of the dendritic molecules [10], leading to alternation of the layers formed by the dendritic matrices with the layers formed by the mesogenic groups.

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3.2. LC dendrimers forming columnar mesophases

Structural polymorphism showing by LC dendrimers of fifth generations deserves a special attention. It will be considered for **G-5(Und-CB)$_{128}$** being the best example of such polymorphism [11]. DSC curve shows two first order phase transitions: at the temperatures 121 °C ($\Delta H = 2.2$ J/g) and 130 °C (ΔH 0.2 J/g) (see Fig. 6 and Attachment 4). Under cooling a weak birefringent grey-yellow mosaic texture is seen just below the clearing point. Cooling below the other phase transition point leads to the formation of a bright colored mosaic texture. Under further cooling the sample below 80 °C it is gradually destroyed. Mosaic texture is characteristic of ordered smectic and columnar mesophases as is known from the literature. Therefore formation of the mosaic texture indicates the presence of more ordered structure then lamellar one presenting in SmA and SmC mesophases. In order to understand the structural types of mesophases formed by the LC dendrimer **G-5(Und-CB)$_{128}$** let us consider SAXS results (Fig. 9).
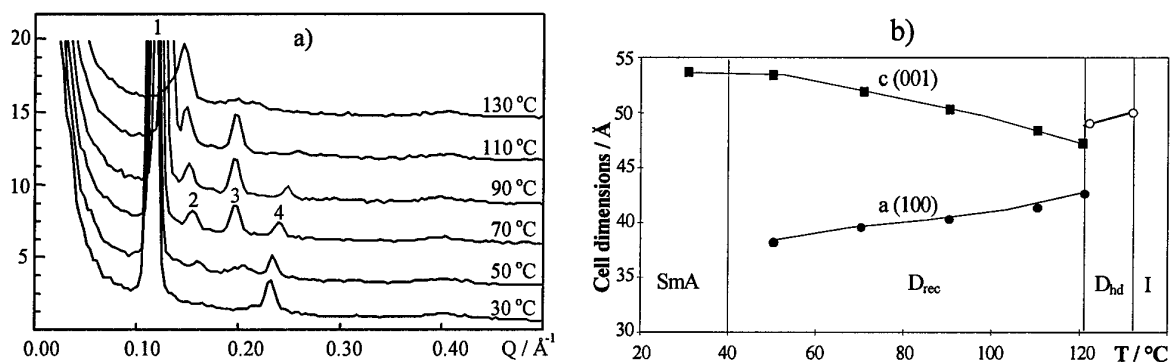

Figure 9. Diffractograms of **G-5(Und-CB)$_{128}$** at different temperatures (a). Temperature dependence of the parameters **a** and **c** of two-dimensional rectangular unit cell of **G-5(Und-CB)$_{128}$** (b).

Up to four different Bragg reflections can be observed on X-ray patterns from an unaligned sample of **G-5(Und-CB)$_{128}$** at different temperatures (Fig. 9a). At 30 °C only peaks 1 and 4 are seen and their Q-values increase with the temperature. They correspond to the 1st and 2nd order reflections from a lamellar structure realizing in SmA mesophase. Their intensities decrease with increasing temperature and they disappear completely at 121 °C. Peaks 2 and 3 appear only above 40 °C and they exist until the transition at 121 °C. Peak 2, however, persists above the transition although it is slightly broader and weaker. The intensities of peaks 2 and 3 are much weaker then the intensity of peak 1 and they have different temperature dependencies. The position of peak 2 is shifted to the lower Q with increasing temperature while peak 3 is temperature independent.

It should be noted that the peaks 1 and 4 tend to partially align parallel to a 9T magnetic field applied to the sample during slow cooling from the isotropic phase. The other peaks do not align. Another broad peak is observed in the mesophases at wide angles. It corresponds to the spacing of about 5 Å, which is typical for phases such as smectic A formed by calamitic molecules and is responsible for the distance between mesogenic groups in the smectic layers.

The results observed can be explained if peaks 1 to 4 index as a two dimensional rectangular unit cell whose dimensions (a , in-plane and c, the layer spacing) vary with temperature as shown in Fig. 9b.

Based on the data described above (Fig. 9) the following structural models of mesophases formed by LC dendrimer $G-5(Und-CB)_{128}$ are suggested (Fig.10). At 30 °C the smectic A (lamellar) structure exists (Fig. 10a), assuming the alternation of the layers consisting of mesogenic groups with layers consisting of the carbosilane dendritic cores. In this case, there is no order within the dendritic layers. They are amorphous due to "softness" of the dendritic part of molecules. At the same time there is a short range order within the layers of mesogenic group which is consistent with a smectic A mesophase. It is likely that in this phase the dendrimer molecules are significantly elongated along the layer normal direction to maximize the mesogen-mesogen interactions (Fig. 10a).

Heating the sample leads to gradual formation of a columnar supramolecular structure in the dendritic layers as a rectangular columnar mesophase D_{rec} (Fig. 10b), which is indicated by appearing of several additional reflections on the X-ray pattern indexed (100), (101), (200), (201) and (202) of two dimensional rectangular cell.[ii] Parameters of this cell depend on the temperature: increasing of the temperature leads to increase of the parameter a (in the layer plain), but decrease of the parameter c (interlayer distance) (Fig. 9b). It can be explained by the following: under increase of the temperature molecules of LC dendrimers become less elongated and their shape become more spherical (Fig. 10b). This tendency to spherical geometry is probably responsible for the gradual break up of the uniform lamellae structure with increasing temperature.

Further heating of the sample leads to a loss of the layers and only a rather disordered hexagonal network of columns persists in the upper mesophase D_{hd} (121 - 135 °C) (Fig. 10c). In this mesophase strong orienting interactions between mesogenic groups are absent and this structure is formed only by the whole molecules of LC dendrimer owing to microphase separation between the aliphatic dendritic part of the molecules and the aromatic mesogenic groups. It is confirmed by a rather large enthalpy of this phase transition (2.1 J/g), while the enthalpy of

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[ii] The fact that there are only the first and second order reflections on the X-ray patterns indicate the presence of low ordered structure. Bragg reflections corresponding the third crystallographic axis (b) are not seen.

the transition $D_{hd} - I$ is significantly less (0.2 J/g). Consequently the internal structure of the supramolecular columns, in our opinion, looks as following. Each column consists of flattened ellipsoidal molecules of LC dendrimers, all mesogenic groups being located on the surface of the columns only. The inner part of the column consists of soft dendritic cores of the molecules of LC dendrimers.
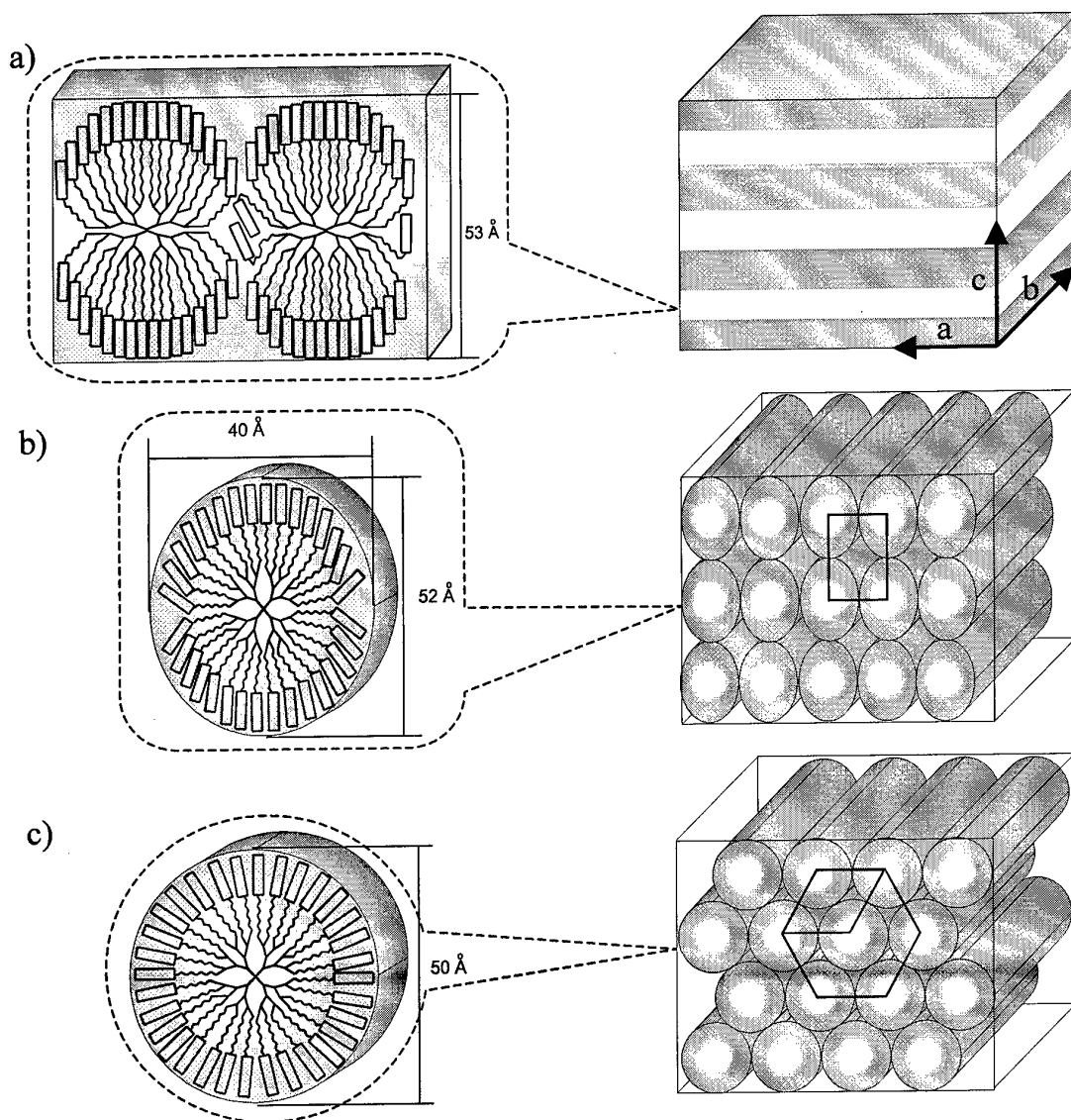

Figure 10. Models of structures formed by LC dendrimer *G-5(Und-CB)$_{128}$* at different temperatures: lamellar structure (SmA mesophase 40 °C) (a); columnar structure with rectangular ordering of ellipsoidal columns (D_{rec} mesophase, 70 °C) (b); columnar structure with hexagonal ordering of rounded columns (D_{hd} mesophase, 130 °C) (c).

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Let us compare now behaviour of LC dendrimers of 4th generation with the same cyanobiphenyl mesogenic groups but with different length of the aliphatic spacer ($-(CH_2)_5-$, and $-(CH_2)_{10}OC-$) [12].

Under cooling the sample of **G-4(Pent-CB)$_{64}$** from the isotropic melt, it forms mosaic texture, annealing of which leads to formation of new unusual textures resembling "monocrystals" or some dendritic structures. It should be noted that the angle between the main axis of all "monocrystals" is equal to 60 $^\circ$C, that is characteristic of hexagonal columnar mesophases. Further cooling leads to gradual distortion of the textures. X-ray patterns shows sharp 1st and 2nd order Bragg reflections in small angles and diffuse peak in wide angles, which is perpendicular to Bragg reflections indicating the presence of SmA mesophase. However, some week sharp satellites of 2nd order Bragg reflection are present at azimuthal angle 30 $^\circ$. All these data as a whole indicate that LC dendrimer **G-4(Pent-CB)$_{64}$** possess more complex supramolecular structure in the mesophase that LC dendrimer **G-4(Und-CB)$_{64}$**, which forms SmA mesophase only. Nevertheless this supramolecular structure is not so good developed as it happens for LC dendrimer of fifth generation **G-5(Und-CB)$_{128}$**, discussed above.

Comparing of LC dendrimers **G-4(Und-CB)$_{64}$** and **G-4(Pent-CB)$_{64}$**, it can be also noted that decrease of the spacer length gives rise to a considerable decrease of the clearing point (by 38 $^\circ$C, from 109 $^\circ$C to 71 $^\circ$C) and to a small decrease of the glass transition temperature (from -21 $^\circ$C to -27 $^\circ$C). At the same time the isotropisation enthalpy is slightly increased (from 3.5 $\div$ 3.9 J/g to 4.2 $\div$ 4.4 J/g).

Thus, the superbranched topology of LC dendrimers predetermines the microphase separation in such systems, which leads to formation of either lamellar or columnar supramolecular structures depending on the generation number. The influence of the chemical nature of the terminal mesogenic groups boils down to the fact that the type of mesogenic group determine specific characteristics of the mesophase formed, such as temperatures and enthalpies of phase transitions, presence or absence of the tilt angle of the mesogenic groups in the smectic layers, etc. The dendritic topology of LC dendrimers is mostly developed for high generations, when supramolecular columnar structures are formed inside the amorphous dendritic layers of the lamellar structure [5, 13].

3.3. Ferroelectric LC dendrimers

Differential scanning calorimetry and polarising optical microscopy studies of the series of LC dendrimers **G-n(Und-PBL)$_m$** reveal only a chiral SmC* phase for all three samples (first to third generations) investigated [4, 14]. All the samples form a broken fan-shaped texture from the room temperature to the clearing point.

This texture is characteristic for the tilted smectic C* phase. Only one endothermic peak which corresponds to transition SmC* → I is observed on the DSC thermograms of this dendrimers (see Attachment 4). Temperatures and enthalpy of the phase transitions, polydispersity and maximum P_s values for these dendrimers are summarized in the Table 1. As is seen from the data presented both the clearing temperatures and the enthalpies of phase transitions of ferroelectric LC dendrimers decreased with increase of the generation number. On the contrary, their glass transition temperatures do not depend on the generation number as it was observed for cyanobiphenyl and methoxyphenyl benzoate containing dendrimers described above.

Table 1.   Phase behaviour, enthalpies of phase transitions, polydispersity and maximum P_s values of the ferroelectric LC dendrimers.

Dendrimer	Phase transitions, °C (in the parenthesis - transition enthalpy, J/g)	M_w/M_n(GPC)	P_s max, nC/cm^2
G-1(Und-PBL)$_8$	g -5 SmC* 175 (10.1) I	1.02	145
G-2(Und-PBL)$_{16}$	g -4 SmC* 167 (8.5) I	1.02	57
G-3(Und-PBL)$_{32}$	g -4 SmC* 158 (6.3) I	1.02	24

Electrooptical investigations have shown that all ferroelectric LC dendrimers synthesized exhibit a clear bistable electro-optical switching in the SmC* phase. The switching between two stable states having opposite P_s directions results in a hysteresis phenomena, as illustrated in Fig. 11 for polarization.
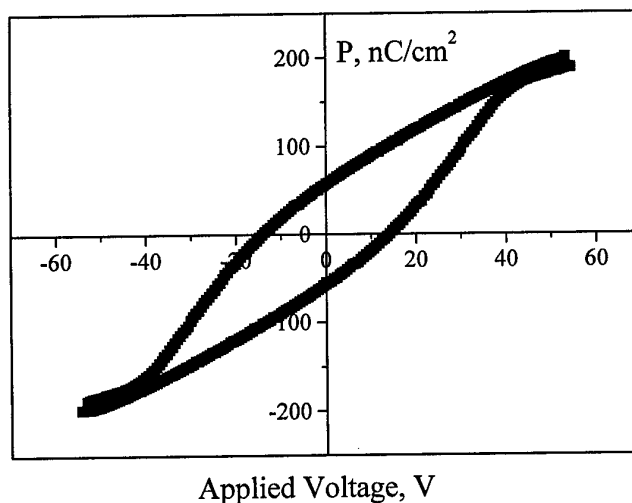

Figure 11. Hysteresis of the polarization in the SmC* phase of **G-2(Und-PBL)$_{16}$**, T = 100°C.

The temperature dependence of the spontaneous polarization for ferroelectric LC dendrimers is shown in Fig. 12. The highest value of P_s, which are shown in the Table 1, were observed at 85°C, 100°C and 115°C for ferroelectric LC dendrimers of the first, second and third generations, respectively. It was impossible to do any correct measurements of the P_s below these temperatures. The error of measurements becomes unambiguous when viscosity of the sample increases. As is seen from the Table 1, the value of the spontaneous polarization decreases with increase of the generation number. This may be explained by reduction of the tilt angle of the mesogenic groups in the smectic layers when generation number of ferroelectric LC dendrimers increases. In order to confirm this suggestion X-ray measurements are in progress now.
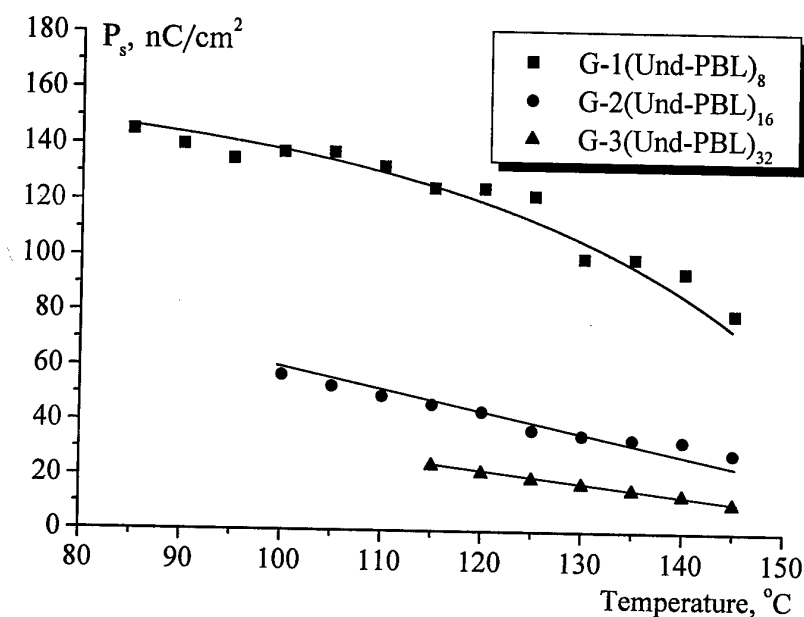

Figure 12.   The temperature dependence of P_s for the FLC dendrimers.

4. Study of molecular properties of LC dendrimers in solutions.

Now let us consider the influence of the generation number and the structure of the terminal mesogenic fragments on the size, shape and oriental mobility of the molecules of carbosilane LC dendrimers synthesized in dilute solutions [15].

The results obtained showed that the values of the intrinsic viscosity $[\eta]$ of LC dendrimers in toluene and chloroform in the limits of the experimental error did not depend on the generation number, i.e. from the molar mass M of the

dendrimers (see Attachment 5) [16]. Constancy of the value [η] in the series of dendrimers investigated allowed to suggest that these molecules behave like solid unpermeable particles, which radius of gyration Rg is proportional to $M^{1/3}$. The dependences of the specific sizes $(R_g/R_{g1})_\eta = (M[\eta])^{1/3}/(M_1[\eta]_1)^{1/3}$ and $(R_g/R_{g1})_{Dif} = D_1/D$ of dendrimer's molecules from $M^{1/3}$, calculated from the data of viscosimetry and translational diffusion respectively are shown in Fig. 13. [iii] In the whole interval of the molecular masses investigated the aggregate of the experimental points was well approximated by the straight line that indicate the good consilience between the molar mass dependences of the relative sizes of dendritic molecules determined by two independent methods. The value of hydrodynamic invariant $A_o = D\eta_o(M[\eta])^{1/3}/T$ (η_o - viscosity of the solvent), calculated from the experimental values of [η], D and M does not depend also from the generation number of dendrimer and was found to be close to the theoretical ones ($A_o = 2.9\times10^{-10}$ erg/Kmol$^{-1/3}$) for compact molecules with the spherical shape.
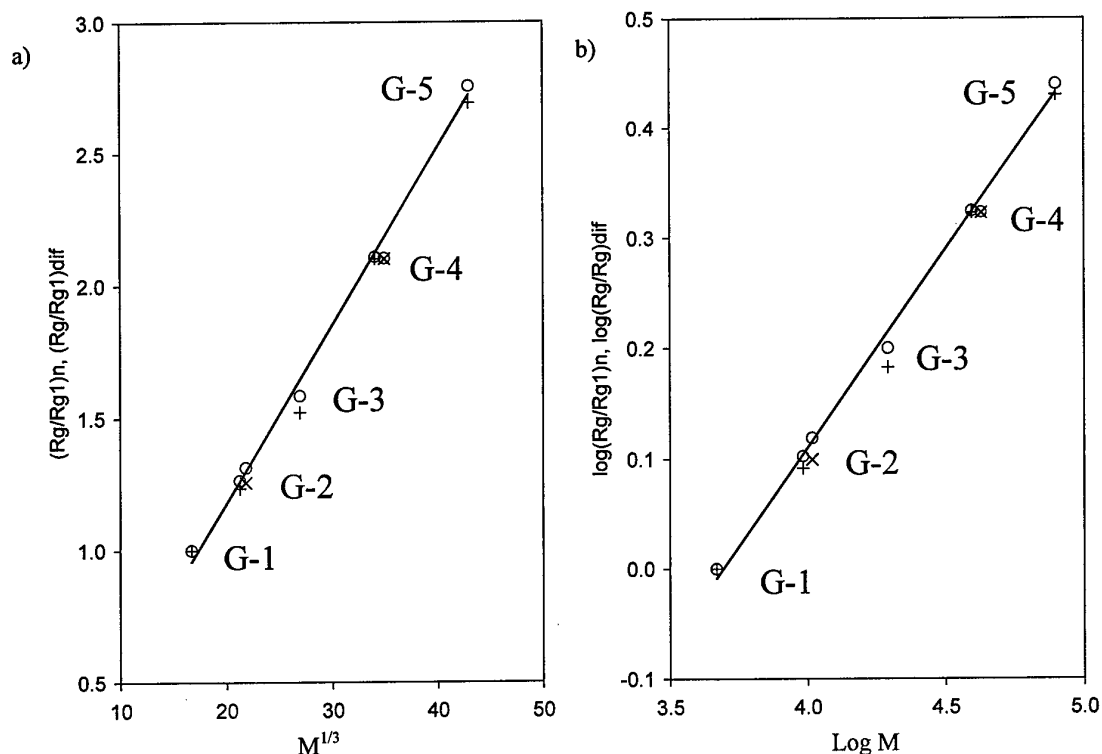

Figure 13. Dependence of the specific sizes $(R_g/R_{g1})_\eta$ (o) and $(R_g/R_{g1})_{dif}$ ($\times$, +) of molecules of LC dendrimers on $M^{1/3}$ (a). Dependence of log $(R_g/R_{g1})_\eta$ (o) and log $(R_g/R_{g1})_{dif}$ ($\times$, +) on log M (b).

[iii] M_1, [η]$_1$ and D_1 are molecular mass, intrinsic viscosity and coefficient of the translational diffusion of the dendrimer of first generation.

The exponent ν, which characterizes the law of molecular sizes change under variation of the molar mass of dendrimers ($Rg \sim M^\nu$), was estimated from the slopes of the straight dependences of $\log(R_g/R_{g1})_{Dif}$ and $\log(R_g/R_{g1})_\eta$ from $\mathrm{Log}(M)$ (Fig. 13). The value $\nu = (0.33\pm0.01)$ received was found to be close to the theoretical one ($\nu = 1/3$) for solid unpermeable particles

Heating of the solution of dendrimers was accompanied by decrease of the value of their intrinsic viscosity $[\eta]$ that is the consequence of a chain structure of their molecules (see Attachment 5). The similar dependences are usually observed for solutions of branched molecules (in particular, for comb-shaped LC polymers) under condition that short range interactions in the chains render the major influence on sizes and shape of the molecules.

Investigation of the electrooptical properties of the solutions of LC dendrimers in toluene, chloroform and tetrachloromethane have shown that specific Kerr constant $K = \Delta n / E^2$ of dendrimers, calculated from the difference in slopes of liner dependences of electric double birefringence (EDB) Δn on the tension of the electric field E squared for the solution and the solvent, did not depend on the generation number [16, 17]. It corresponds by the order of magnitude to the values of K of their low molar mass analogues (see Attachment 5). So, for example, the value of the Kerr constant for **G-3(Und-CB)₃₂** in toluene was found to be 2.68×10^{-10} SGSE units, and for the cyanobiphenyl in toluene it is equal to 6.39×10^{-10} SGSE units. This fact, as well as absence of the radio frequency dispersion of the Kerr effect shows that EDB in the solutions of LC dendrimers is induced by a small-scaled orientation of the terminal mesogenic fragments, like it happens in comb-shaped LC polymers.

The results obtained allow to conclude, that both hydrodynamic and electrooptical properties of the LC dendrimers investigated do not actually depend on the generation number. However, the dependence of hydrodynamic and electrooptical properties on the chemical nature of the terminal mesogenic groups is different. The former do not depend on the type of mesogenic groups, that allows to generalize the conclusions made for the whole class of LC dendrimers with terminal mesogenic groups. The latter, vice versa, are determined by the electrooptical properties of the mesogenic groups.

The results presented above allows to suggest the following possible application area LC dendrimers with terminal mesogenic groups. At the present time usage of dendrimers as «dendritic boxes» for encapsulation of different large molecules is described in the literature. Presence of the terminal groups, which are easily oriented in the electric field, in LC dendrimers can lead to creation of specific «dendritic boxes» with controlled permeability of the encapsulated molecules depending on the applied electric field. In particular, it should be

possible to create «switchable dendritic boxes» or «dendritic switchers» which could control the local concentration of the encapsulated substances under the action of the electric (or magnetic) field.

5. Conclusions and recommendations for future work and applications.

To sum up the work under the Project, the following conclusions can be made:

1. The new universal approach to the synthesis of carbosilane LC dendrimers has been elaborated. It allows to vary the general structural constituents of these complex molecular systems such as generation number of the dendritic matrix, length of the aliphatic spacers and chemical nature of the terminal mesogenic groups.

2. Five generations of carbosilane LC dendrimers with 8, 16, 32, 64 and 128 terminal cyanobiphenyl, methoxyphenyl benzoate and the derivatives of ethyl-L-lactate mesogenic groups have been synthesized. It was confirmed that all LC dendrimers synthesized were individual monodisperse compounds with beforehand expected molecular structure.

3. It was shown that all mesogen-containing dendrimers obtained performed a thermodynamically stable LC state. The temperature interval of the existence of LC state, thermodynamic parameters of phase transitions and structural types of LC mesophases formed were determined. It was found that all LC dendrimers investigated form smectic A and C mesophases, a lamellar structure of which is alternation of the layers of mesogenic groups with the layers consisting of soft carbosilane dendritic matrices. Models of packing of mesogenic groups in LC mesophases have been suggested. Differences in the structure of cyanobiphenyl and methoxyphenyl benzoate containing dendrimers have been revealed.

4. For the first time correlation between the molecular structure of LC dendrimers with terminal mesogenic groups (i.e. generation number, molar mass, type of the mesogenic groups and the spacer length) and thermodynamic parameters (temperature, enthalpy and entropy) of the transition from LC state to isotropic melt has been investigated. It was found that increase of the generation number leads to increase of the temperature, but decrease of the enthalpy and the entropy of this phase transition. An explanation of this phenomenon has been suggested.

5. For the first time formation of supramolecular columnar mesophases (with rectangular (D_{rec}) and hexagonal (D_{hex}) arrangement of columns) has been

discovered for LC dendrimers of high generations. Criteria for formation of these mesophases have been determined both from the viewpoint of the molecular structure of LC dendrimers and from the viewpoint of the thermodynamic conditions. It was found that decrease of the spacer length lead to formation of similar LC supramolecular structures for lower generations of LC dendrimers. It was shown that the columnar mesophases were gradually formed from the lamellar ones under the heating of the sample without any observable phase transition and they were thermodynamically stable phases. Models of packing of LC dendrimers' molecules in these supramolecular phases have been suggested.

6. For the first time a series of carbosilane ferroelectric liquid crystalline dendrimers has been synthesized and investigated. All these LC dendrimers exhibit the chiral smectic C mesophase in a broad temperature range. The highest spontaneous polarization is about 140 nC/cm^2 for the LC dendrimer of the first generation and is reduced with increase of generation number.

7. Investigation of hydrodynamic and electrooptical properties of dilute solutions of LC dendrimers allowed to establish quantitative correlation between the sizes of LC dendrimers molecules and their molar mass ($R_g \sim M^v$). The value v = (0.33±0.01) received turned to be close to the theoretical one for solid unpermeable particles. It means, that hydrodynamic properties of carbosilane LC dendrimers are similar to that of solid unpermeable particles. However, chain character of the structure of LC dendrimers appears in the temperature changes of the viscosity and small scaled mechanism of their orientation in the electric field.

The results, summarized above indicate that LC dendrimers are a new class of liquid crystals forming some new unexpected structures and possessing unusual properties. Investigation of them has just only began and this Project presents only the first steps in the systematical study of carbosilane LC dendrimers with terminal mesogenic groups. Of course, short duration of the Project has not allowed to make full systematic investigation, nevertheless, even the first results received looks very interesting and promising as presented above. They allow suggesting the following possible areas of application of LC dendrimers:

1. As molecular weights standards.
All the LC dendrimers synthesized were proved to be monodisperse individual substances with given molar masses ranges from 5,000 to 80,000. They are soluble in many polar organic solvent such as THF, trichloromethane, etc. Solubility in less polar solvents (i.e. in toluene) decreases with increasing of the generation number for LC dendrimers with cyanobiphenyl mesogenic groups.

However, using of less polar mesogenic groups (i.e. cholesteryl) makes them soluble in toluene and even in non-polar solvents such as hexane. Therefore, LC dendrimers can be used as molecular weight standards in many organic solvents to apply, for instance, in GPC, HPLC, etc.

2. As size standards in nanoscale range.

All LC dendrimers are molecules-particles of spherical shape with definite size due to specific molecular structure leading to tree dimensional molecular architecture of spherical symmetry. Size of such molecules is determined mostly by the generation number, as well as by the spacer length between the terminal mesogenic groups and the carbosilane dendritic core. Elaborated synthetic route allows to produce such molecules-particles with estimated sizes ranging from approx. 2 to 10 nm. Theoretically the upper limit of the molecule size can be extended up to 45 nm in the case of using of large spacers (i.e. undecylenic) between the branching points in the dendritic matrix. Such work was not planned in the reporting period of the Project, but can be done in the future.

3. As "switchable molecular boxes".

"Dendritic boxes" as is know from the literature can encapsulate large molecules inside the dendritic molecules. Results of the investigation of hydrodynamic and electrooptical properties of LC dendrimers in solutions allows to suggest creation of "switchable molecular boxes". Presence of the terminal mesogenic groups should allow to control or switch a permeability of "dendritic boxes" by the action of an external field (electric or, possibly, magnetic). Such suggestion was made, because of the following. On the one hand, LC dendrimers behave in the dilute solutions like solid unpermeable particles. It means, that the outer shell of LC dendrimers is rather dense. On the other hand, terminal mesogenic groups orient in the electric field independently each other that indicate on the presence of some free space in the outer shall the molecules at least under applying of the electric field. Bering in mind the tendency of LC dendrimers to form layered strictures, some microsegregation of the molecule should exists at least in some bad solvents. It would induce some large "holes" in the dense outer shell of the molecule, making it permeable for encapsulated molecules under the action of the electric field. Of course, this is only the suggestion that needs further checking, but the results received indicate that there is a great chance that it should work. It would be good to check it both theoretically by computer simulations and experimentally.

It should be noted, that only the results of those investigations, which were completed and interpreted by now, were included in the Final report. Some of the

investigations are in progress now (i.e. synthesis and study of photochromic and optically active LC dendrimers, AFM investigations of the superstructures of LC dendrimers and some others) and they were not included in the Final report because of incompleteness[iv].

List of publications

1. Ponomarenko S.A., Rebrov E.A., Boiko N.I., Muzafarov N.G., Shibaev V.P., Synthesis of five generations of carbosilane dendrimers with terminal cyanobiphenyl groups. // *Vysokomol. Soedin., Ser. A*, 1998, V. 40, No. 8, P. 1253 - 1265 (in Russian); *Polymer Science, Ser.A*, 1998, V. 40, No. 8, P. 763-775 (in English).
2. Ponomarenko S.A., Boiko N.I., Rebrov E.A., Muzafarov A.M., Whitehouse I.J., Richardson R.M., Shibaev V.P. Synthesis, phase behaviour and structure of liquid crystalline dendrimers with methoxyphenyl benzoate terminal mesogenic groups // *Mol. Cryst. Liq. Cryst.*, 1999, V. 332, P. 2553-2560
3. N.I. Boiko, Invited lecture: "Liquid crystalline carbosilane dendrimers of regular structure: influence of molecular architecture of the phase behavior and properties" // *Proceedings of the 4th Russian Symposium on Liquid Crystalline Polymers*, Klyaz'ma, January 25-28, 1999, P. 15
4. N.I. Boiko, X. Zhu, R. Vinokur, E.A. Rebrov, A.M. Muzafarov, V.P Shibaev. New carbosilane ferroelectric liquid crystalline dendrimers. // *Mol. Cryst. Liq. Cryst.* (submitted).
5. Ponomarenko S.A., Boiko N.I., Rebrov E.A., Muzafarov A.M., Whitehouse I.J., Richardson R.M., Shibaev V.P. Carbosilane liquid crystalline dendrimers: from molecular architecture to supramolecular nanostructures. // *J. Am. Chem. Soc.* (submitted).
6. Ponomarenko S.A., Boiko N.I., Rebrov E.A., Muzafarov A.M., Whitehouse I.J., Richardson R.M., Shibaev V.P., Poster presentation: "Synthesis, phase behaviour and structure of liquid crystalline dendrimers with terminal mesogenic groups", *Abstracts of 17th International Liquid Crystal Conference*, Strasbourg, France, July 19-24, 1998, P4-051
7. Shibaev V.P., Ponomarenko S.A., Boiko N.I., Rebrov E.A., Muzafarov A.M., Whitehouse I.J., Richardson R.M., Poster presentation: "Liquid crystalline dendrimers with terminal mesogenic groups: synthesis, thermal behavior and structure", *Preprints of 37th International Symposium on Macromolecules*, Gold Coast, Australia, July 12-17, 1998, P. 773

[iv] Actually in the Formal Proposal these investigations were planned for the second and third year of the research work while this Contract had a one-year duration.

8. R.M. Richardson, I.J. Whitehouse, S.A. Ponomarenko, N.I. Boiko, V.P. Shibaev. Poster presentation: "X-ray diffraction from liquid crystalline carbosilane dendrimers", *Abstracts of 17th International Liquid Crystal Conference*, Strasbourg, France, July 19-24, 1998, P2-151

9. R.M. Richardson, I.J. Whitehouse, S.A. Ponomarenko, N.I. Boiko, V.P. Shibaev. X-ray Diffraction from Liquid Crystalline Carbosilane Dendrimers. // *Mol. Cryst. Liq. Cryst.*, 1999, V.330, P.1411-1419.

10. Shibaev V.P., Ponomarenko S.A., Boiko N.I., Rebrov E.A., Muzafarov A.M., Whitehouse I.J., Richardson R.M., Invited lecture: "Liquid crystalline dendrimers as a new type of intramolecular phase-separated and self-assembled nanostructure materials", *Abstracts of International Workshop "Chemistry and Characterization of Mesophase materials"*, Bayreuth, Germany, October 4-6, 1998, P. L7

11. Richardson R.M., Ponomarenko S.A., Boiko N.I., Shibaev V.P. Liquid crystalline dendrimer of the fifth generation: from lamellar to columnar structure in thermotropic mesophases. // *Liquid Crystals*, 1999, V. 26, No 1, P. 101-106.

12. Ponomarenko S.A., Boiko N.I., Rebrov E.A., Whitehouse I.J., Richardson R.M., Muzafarov A.M., Shibaev V.P., Poster presentation: "Liquid crystalline dendrimers with cyanobiphenyl mesogenic groups: from lamellar to columnar phases" // *Proceedings of the 4th Russian Symposium on Liquid Crystalline Polymers*, Klyaz'ma, January 25-28, 1999, P. 82.

13. Ponomarenko S.A., Boiko N.I., Rebrov E.A., Muzafarov A.M., Whitehouse I.J., Richardson R.M., Shibaev V.P., Poster presentation: "Synthesis and structural peculiarities of liquid crystalline carbosilane dendrimers", *Abstracts of European Liquid Crystal Conference*, Crete, Greece, April 25-30, 1999, P3-091.

14. N.I. Boiko, X. Zhu, R. Vinokur, E.A. Rebrov, A.M. Muzafarov, V.P Shibaev. Poster presentation: " New carbosilane ferroelectric liquid crystalline dendrimers", *Abstracts of European Liquid Crystal Conference*, Crete, Greece, April 25-30, 1999.

15. Lezov A.V., Mel'nikov A.B., Polushina G.E., Ponomarenko S.A., Boiko N.I., Rjumtsev E.I., Shibaev V.P., Poster presentation: "Molecular properties of liquid-crystalline carbosilane dendrimers", *Abstracts of 17th International Liquid Crystal Conference*, Strasbourg, France, July 19-24, 1998, P3-125

16. Lezov A.V., Mel'nikov A.B., Polushina G.E., Ponomarenko S.A., Boiko N.I., Kossmehl E., Ryumtsev E.I., Shibaev V.P. Dualism in hydrodynamic behaviour of liquid crystalline carbosilane dendrimers in dilute solutions // *Doklady Academii Nauk,* 1998, V. 252, No. 5. P. 638-642 (in Russian); *Doklady of Physical Chemistry*, 1998, V. 252, No. 5. P. 138-142 (in English).

17. Rjumtsev E.I., Evlampieva N.P., Lezov A.V., Ponomarenko S.A., Boiko N.I., Shibaev V.P. Kerr effect in solutions of carbosilane dendrimers with the terminal mesogenic groups. // *Liquid Crystals*, 1998, V. 25, No. 4, P. 475-479.

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3) **Aziz M. Muzafarov** -   Doctor of Sciences, Leading Researcher
4) **Evgeny A. Rebrov** -   Ph.D., Senior Researcher
5) **Sergey A. Ponomarenko** -   Ph. D., Junior Researcher (got Ph.D. in April 1999 after defending his Dissertation under the title "Liquid crystalline carbosilane dendrimers: synthesis, structure and properties")
6) **Svetlana A. Amelechina** -   Technician.

List of attachments

Attachment 1. 250 MHz ^{1}H NMR spectra of some new compounds. Asterisk refers to the signal of $CDCl_3$ (7.25 ppm) (**9 pages**)

1) ^{1}H NMR spectra of the compound **G-3(All)$_{32}$**.
2) ^{1}H NMR spectra of the compound **G-4(All)$_{64}$**.
3) ^{1}H NMR spectra of the compound **G-5(All)$_{128}$**.
4) ^{1}H NMR spectra of the compound **H-Si-Und-CB**.
5) ^{1}H NMR spectra of the compound **Und-PBL**.
6) ^{1}H NMR spectra of the compound **G-3(Und-CB)$_{32}$**.
7) ^{1}H NMR spectra of the compound **G-4(Und-CB)$_{64}$**.
8) ^{1}H NMR spectra of the compound **G-5(Und-CB)$_{128}$**.

Attachment 2. GPC traces of some different carbosilane dendrimers synthesized. (**2 pages**).

1) GPC traces of carbosilane dendrimers with the terminal allyl groups **G-n(All)$_m$**: 1 - **G-1(All)$_8$** , 2 - **G-2(All)$_{16}$** , 3 - **G-3(All)$_{32}$** , 4 - **G-4(All)$_{64}$** , 5 - **G-5(All)$_{128}$** ; (10^3 Ultrastiragel 8×300 mm column, detector – refractometer).

2) GPC traces of carbosilane dendrimers with the terminal cyanobiphenyl mesogenic groups: 1 - **G-1(Und-CB)$_8$** , 2 - **G-2(Und-CB)$_{16}$** , 3 - **G-3(Und-CB)$_{32}$** , 4 - **G-4(Und-CB)$_{64}$** , 5 - **G-5(Und-CB)$_{128}$** (10^3 Ultrastiragel 19×300 mm column, detector – UV spectrophotometer)

Attachment 3. Molecular mass parameters of all the dendrimers synthesized calculated from the GPC data. (**1 page**)

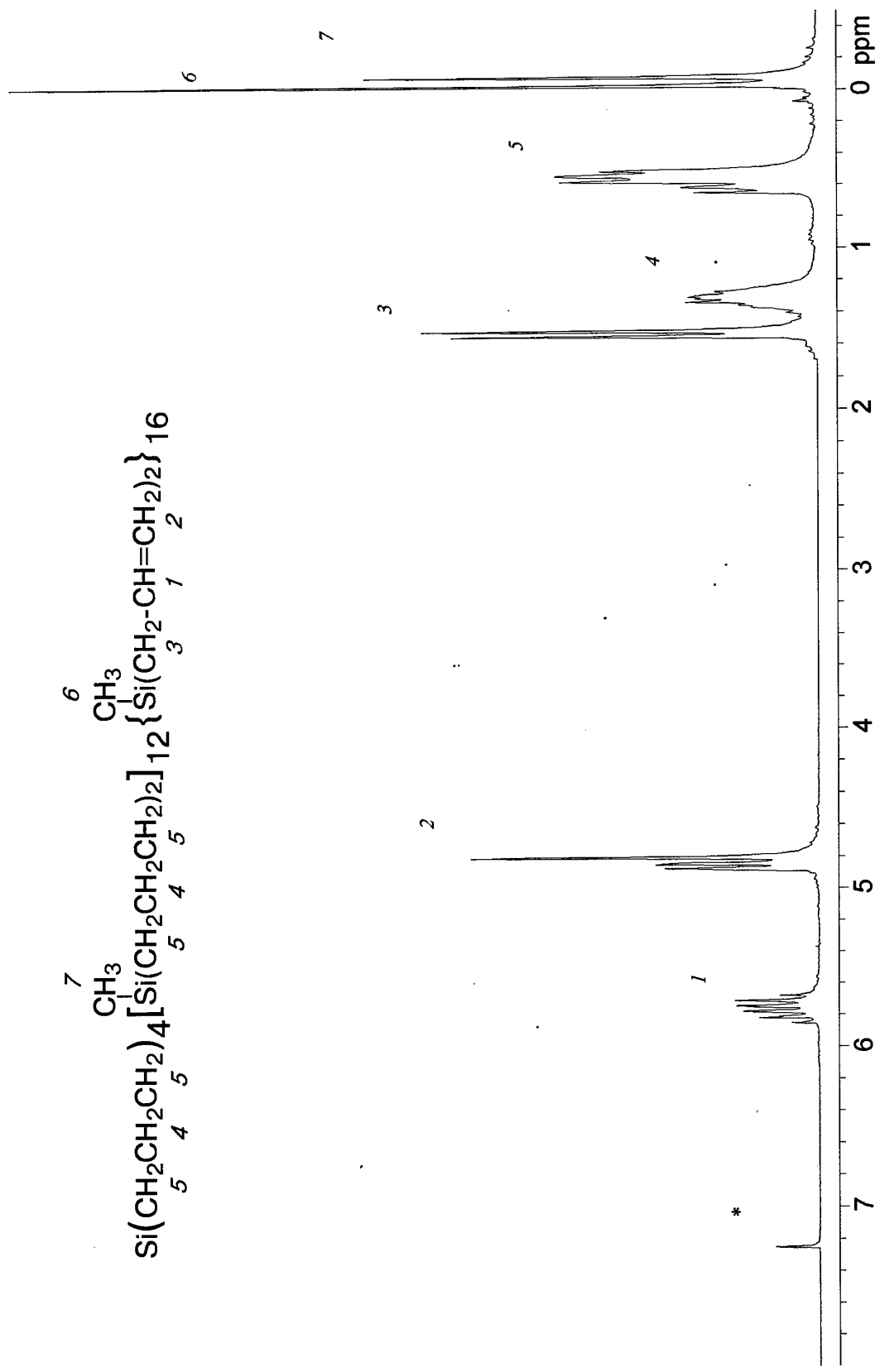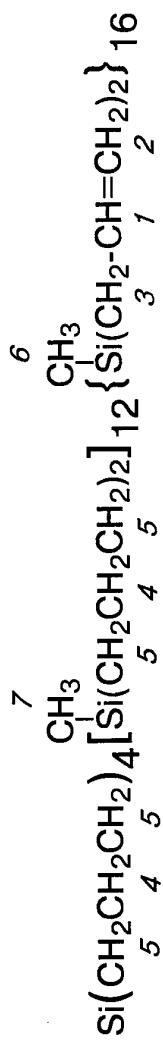Attachment 4. DSC traces of some LC dendrimers investigated. (**3 pages**)

1) DSC traces of LC dendrimers **G-n(Und-MPhB)$_m$** : 1 - **G-1(Und-MPhB)$_8$** , 2 – **G-2(Und-MPhB)$_{16}$** , 3 - **G-3(Und-MPhB)$_{32}$** , 4 - **G-4(Und-MPhB)$_{64}$** , 5 - **G-5(Und-MPhB)$_{128}$**
2) Second heating (a) and first cooling (b) DSC traces of LC dendrimers **G-n(Und-CB)$_m$** : 1 - **G-1(Und-CB)$_8$** , 2 – **G-2(Und-CB)$_{16}$** , 3 - **G-3(Und-CB)$_{32}$** , 4 - **G-4(Und-CB)$_{64}$** , 5 - **G-5(Und-CB)$_{128}$**
3) DSC traces of LC dendrimers **G-n(Und-PBL)$_m$** : 1 - **G-1(Und-PBL)$_8$** , 2 – **G-2(Und-PBL)$_{16}$** , 3 - **G-3(Und-PBL)$_{32}$** .

Attachment 5. Hydrodynamic and electrooptical properties of carbosilane LC dendrimers in toluene (tol) and chloroform (chl). (**1 page**).
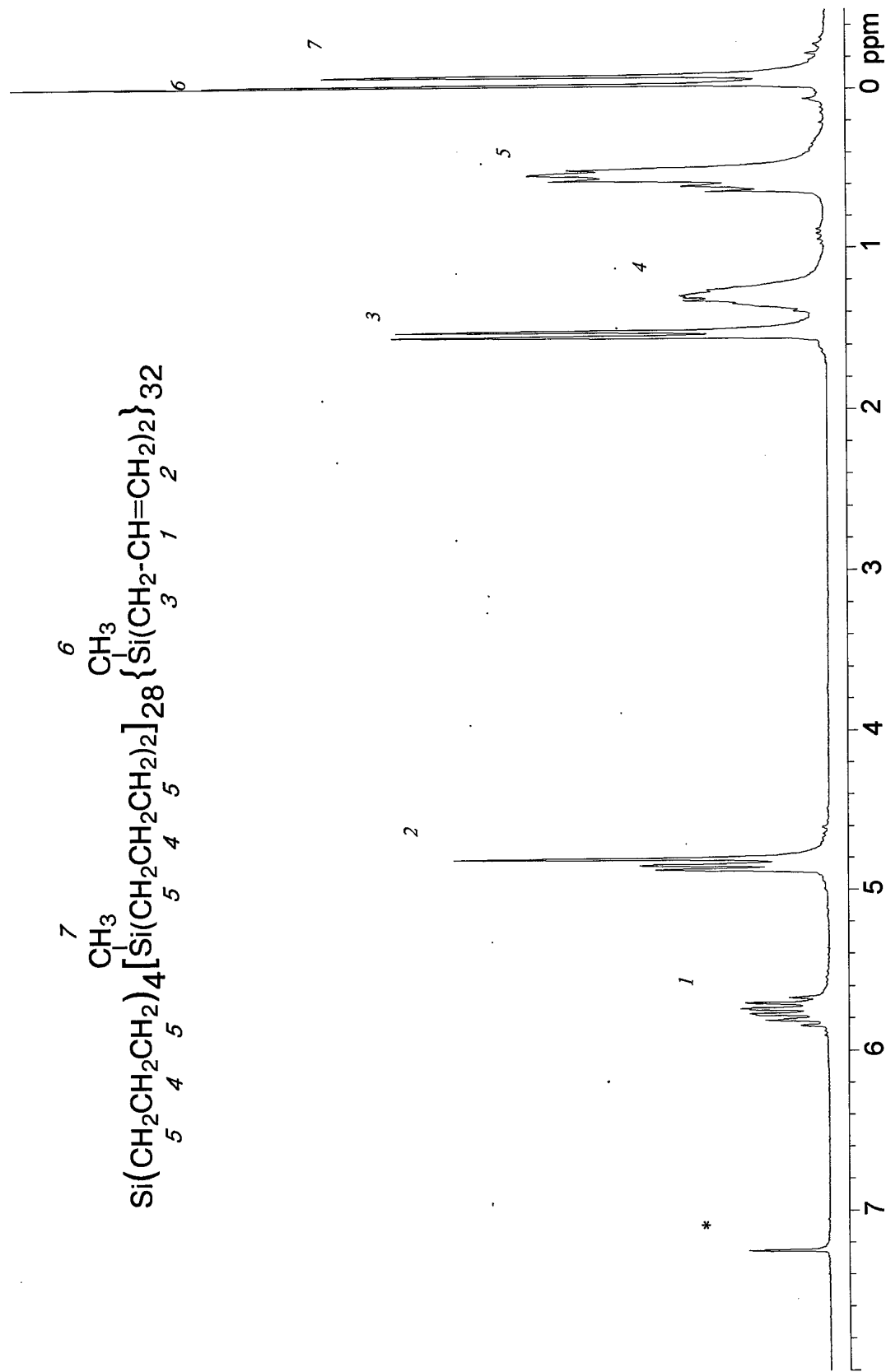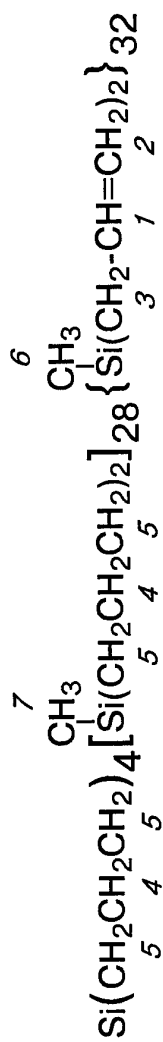
Attachment 1. 250 MHz ^{1}H NMR spectra of some new compounds.
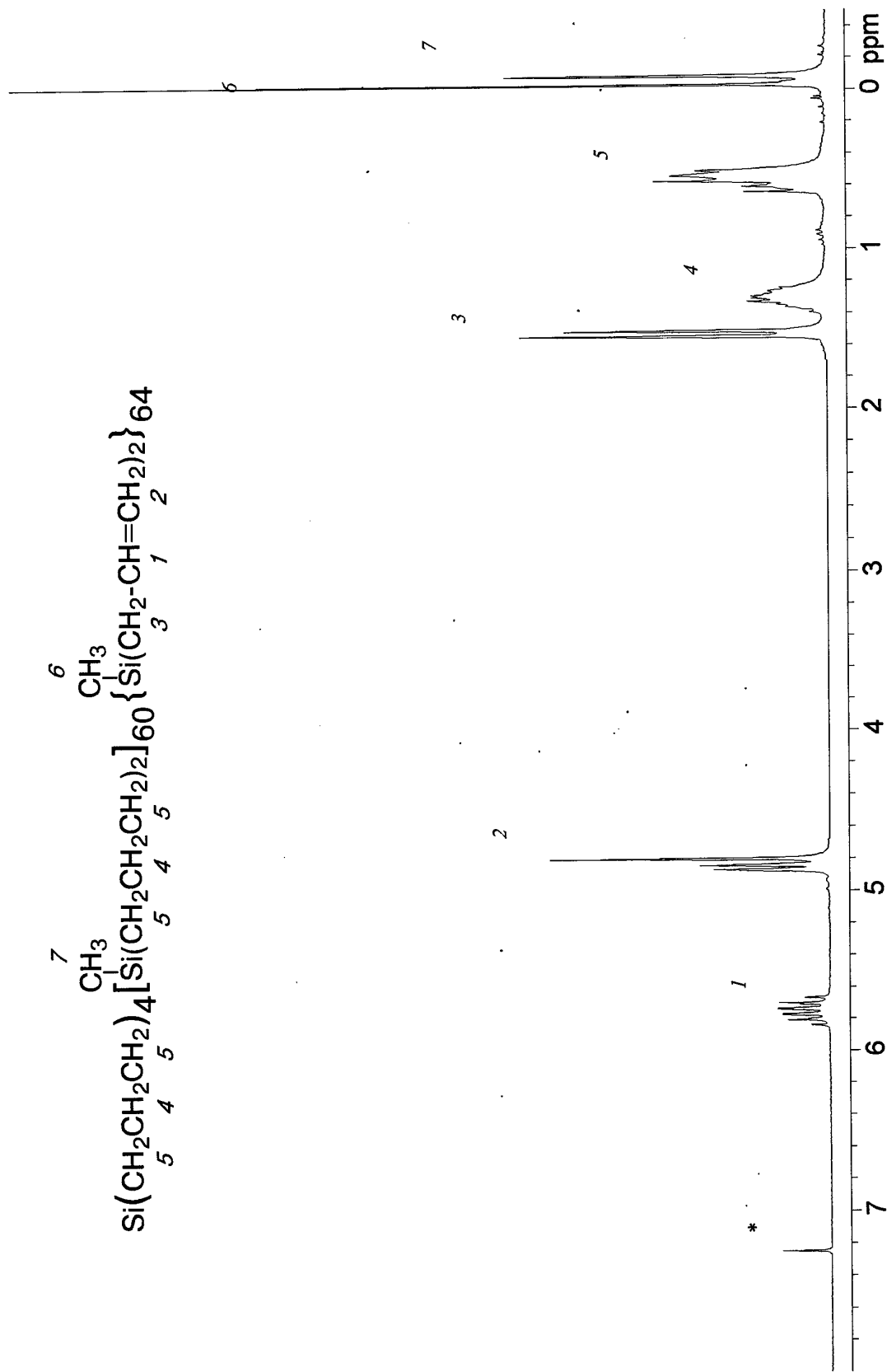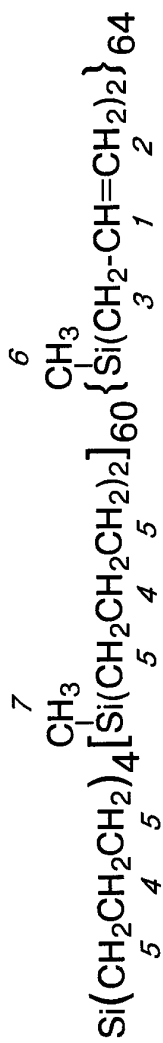Asterisk refers to the signal of CDCl$_3$ (7.25 ppm)

1) ^{1}H NMR spectra of the compound **G-3(All)$_{32}$.**

2) ^{1}H NMR spectra of the compound **G-4(All)$_{64}$.**

3) ^{1}H NMR spectra of the compound **G-5(All)$_{128}$.**

4) ^{1}H NMR spectra of the compound **H-Si-Und-CB.**

5) ^{1}H NMR spectra of the compound **Und-PBL.**

6) ^{1}H NMR spectra of the compound **G-3(Und-CB)$_{32}$.**

7) ^{1}H NMR spectra of the compound **G-4(Und-CB)$_{64}$.**
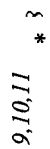
8) ^{1}H NMR spectra of the compound **G-5(Und-CB)$_{128}$.**

$$Si(CH_2CH_2CH_2)_4\left[\overset{\overset{\displaystyle 6}{CH_3}}{\underset{}{Si}}(CH_2CH_2CH_2)_2\right]_{12}\left\{\overset{\overset{\displaystyle 6}{CH_3}}{\underset{}{Si}}(CH_2-CH=CH_2)_2\right\}_{16}$$

1) 250 MHz ^{1}H NMR spectra of the compound **G-3(All)$_{32}$**

$$\underset{5}{\text{Si}}\underset{4\ 5}{(\text{CH}_2\text{CH}_2\text{CH}_2)_4}\left[\underset{3}{\text{Si}}\underset{4\ 5}{(\text{CH}_2\text{CH}_2\text{CH}_2)_2}\right]_{28}\left\{\underset{1}{\text{Si}}\underset{3}{(\text{CH}_2}\text{-}\underset{1}{\text{CH}}=\underset{2}{\text{CH}_2})_2\right\}_{32}$$

7 CH₃ (on first Si)
6 CH₃ (on {Si} group)

2) 250 MHz ^{1}H NMR spectra of the compound **G-4(All)$_{64}$**

Si(CH$_2$CH$_2$CH$_2$)$_4$[Si(CH$_2$CH$_2$CH$_2$)$_2$]$_{60}$\{Si(CH$_2$-CH=CH$_2$)$_2$\}$_{64}$
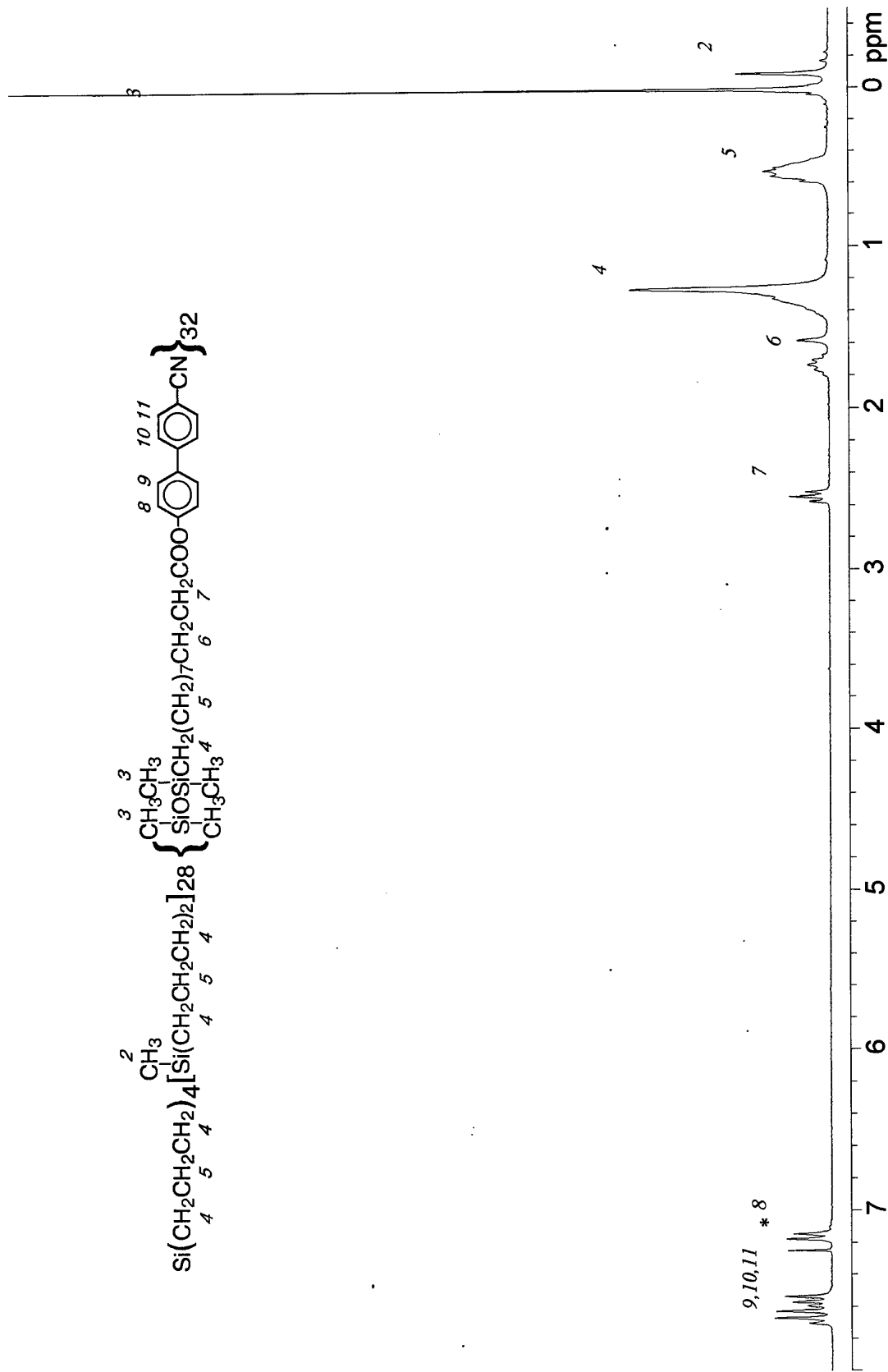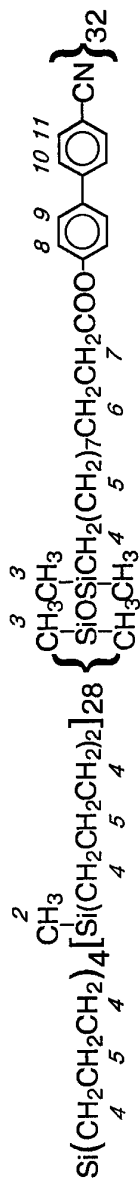
CH$_3$ (7)

CH$_3$ (6)

3) 250 MHz ^{1}H NMR spectra of the compound **G-5(All)$_{128}$**

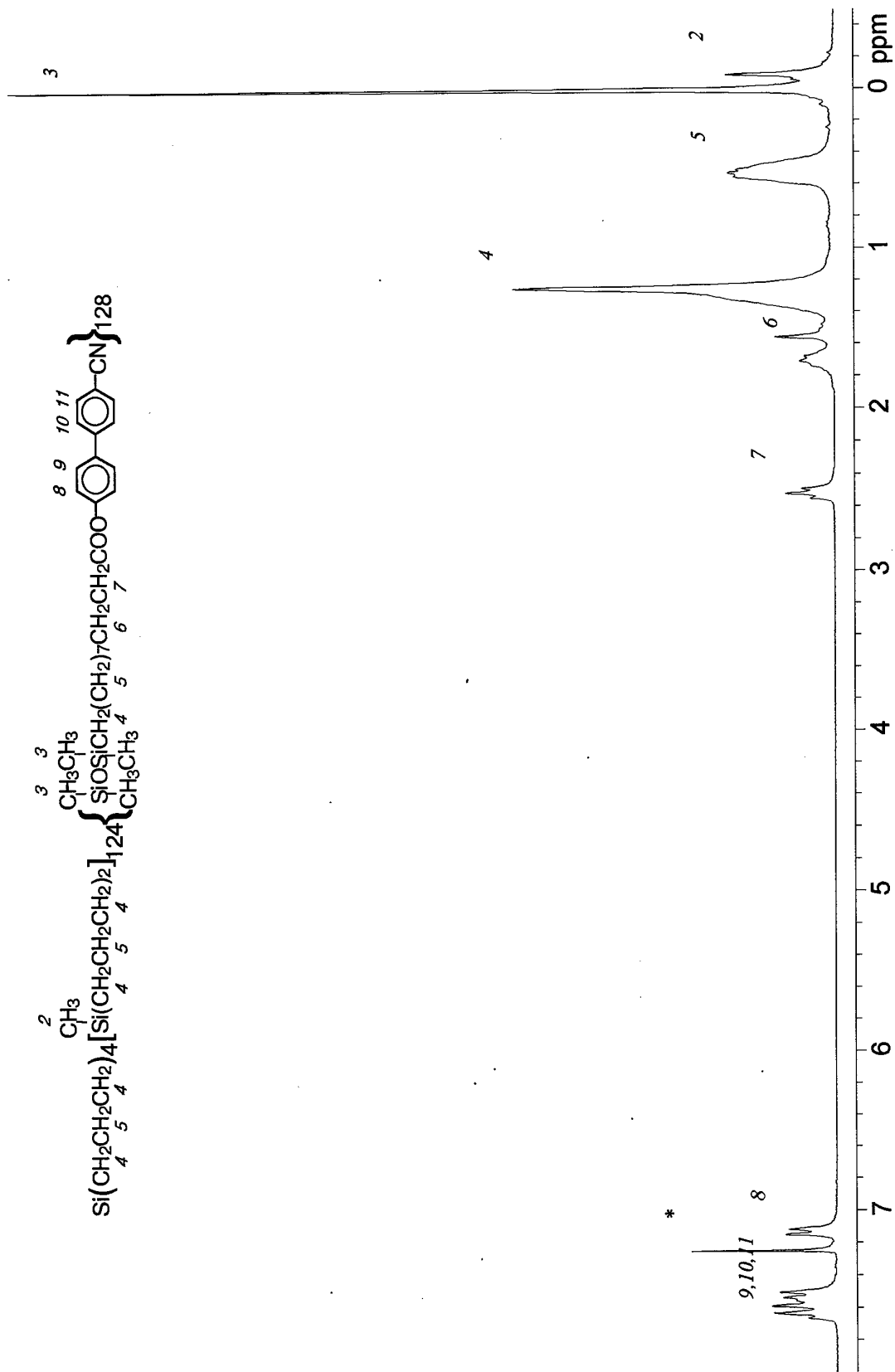4) 250 MHz ^{1}H NMR spectra of the compound **H-Si-Und-CB**
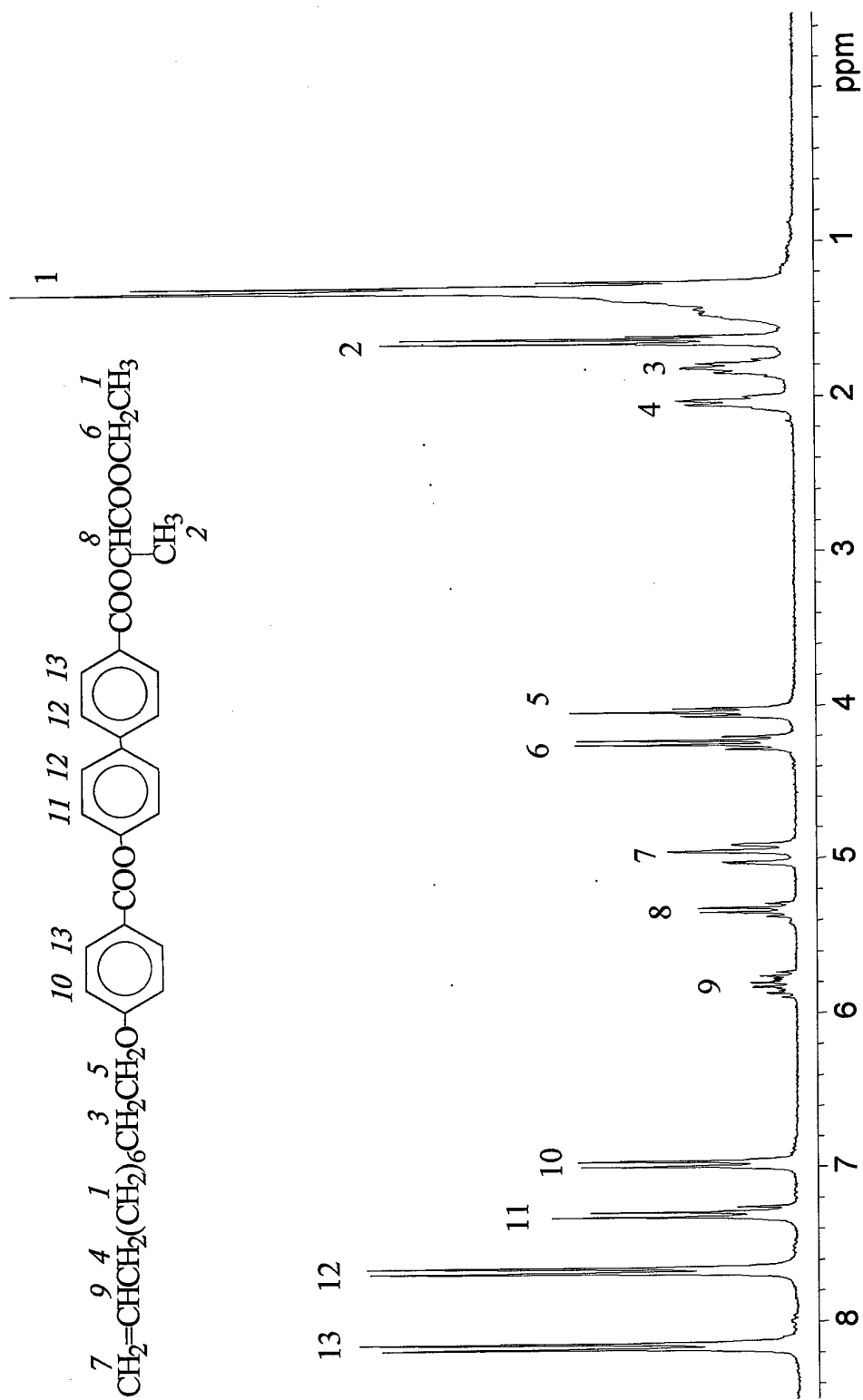
5) 250 MHz ^{1}H NMR spectra of the compound Und-PBL

Si(CH$_2$CH$_2$CH$_2$)$_4$[Si(CH$_2$CH$_2$CH$_2$CH$_2$)$_2$]$_{28}$ { SiOSiCH$_2$(CH$_2$)$_7$CH$_2$CH$_2$COO—⟨⟩—⟨⟩—CN }$_{32}$

6) 250 MHz ^{1}H NMR spectra of the compound **G-3(Und–CB)**$_{32}$

Si(CH₂CH₂CH₂)₄[Si(CH₂CH₂CH₂)₂]₆₀{SiOSiCH₂(CH₂)₇CH₂CH₂COO—⟨phenyl⟩—⟨phenyl⟩—CN}₆₄

$Si(CH_2CH_2CH_2)_4[Si(CH_2CH_2CH_2)_2]_{60}\{SiOSiCH_2(CH_2)_7CH_2CH_2COO-C_6H_4-C_6H_4-CN\}_{64}$

7) 250 MHz ^{1}H NMR spectra of the compound **G-4(Und-CB)₆₄**
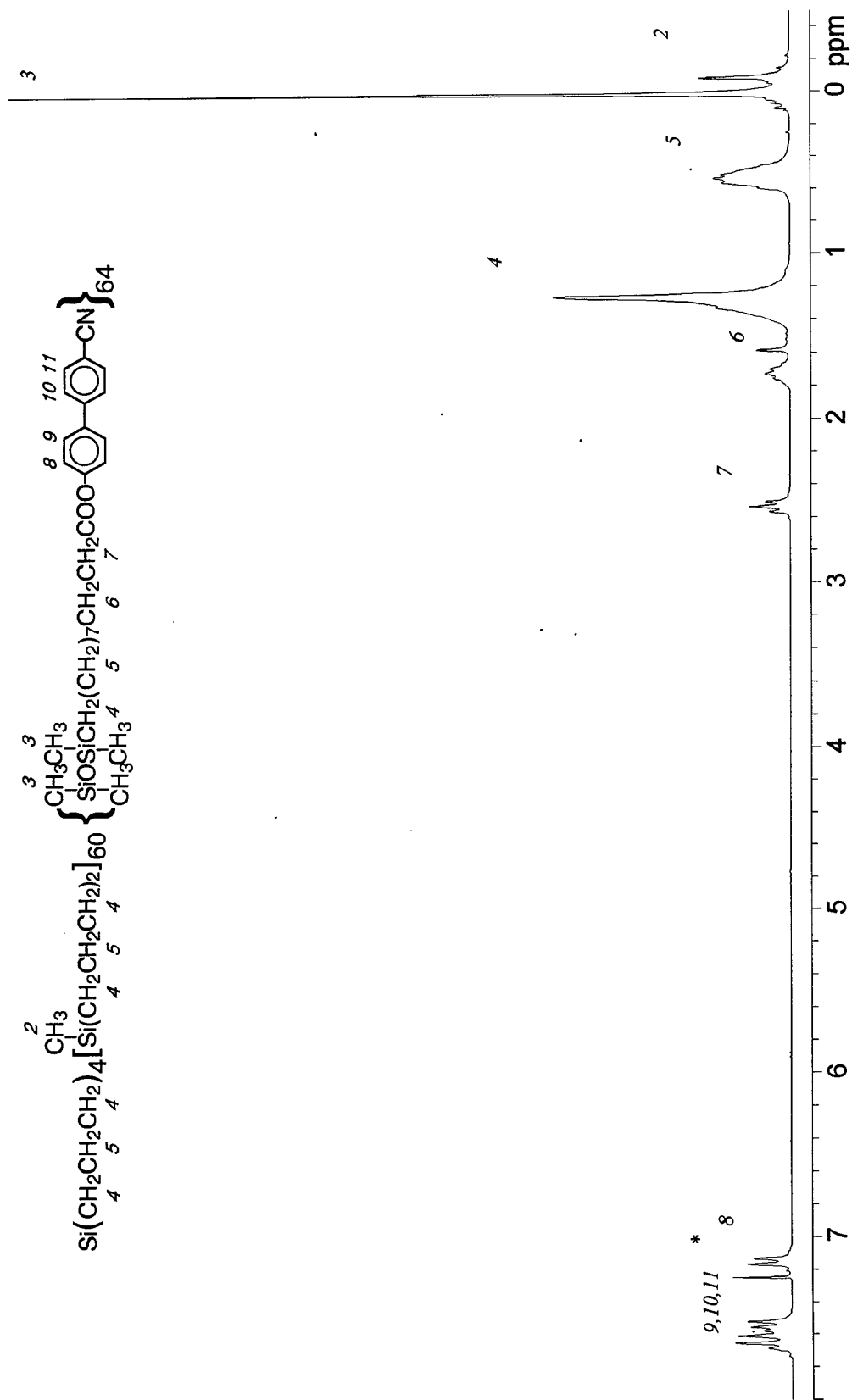
8) 250 MHz ^{1}H NMR spectra of the compound **G-5(Und-CB)**$_{128}$

Attachment 2. GPC traces of some different carbosilane dendrimers synthesized.
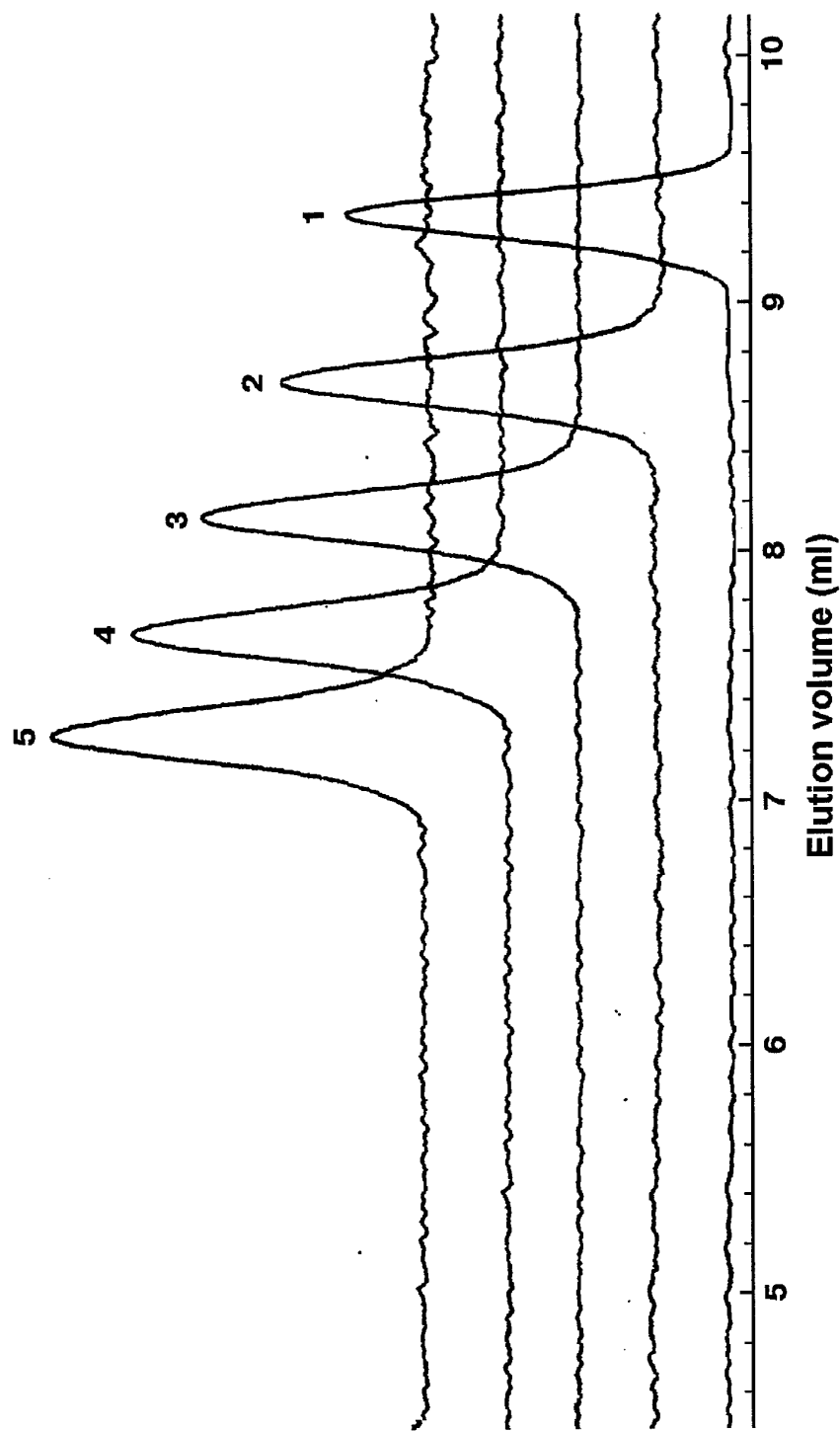
1) GPC traces of carbosilane dendrimers with the terminal allyl groups **G-n(All)$_m$**: 1 - **G-1(All)$_8$** , 2 - **G-2(All)$_{16}$** , 3 - **G-3(All)$_{32}$** , 4 - **G-4(All)$_{64}$** , 5 - **G-5(All)$_{128}$** ; (10^3 Ultrastiragel 8×300 mm column, detector – refractometer)

Attachment 2. GPC traces of some different carbosilane dendrimers synthesized.
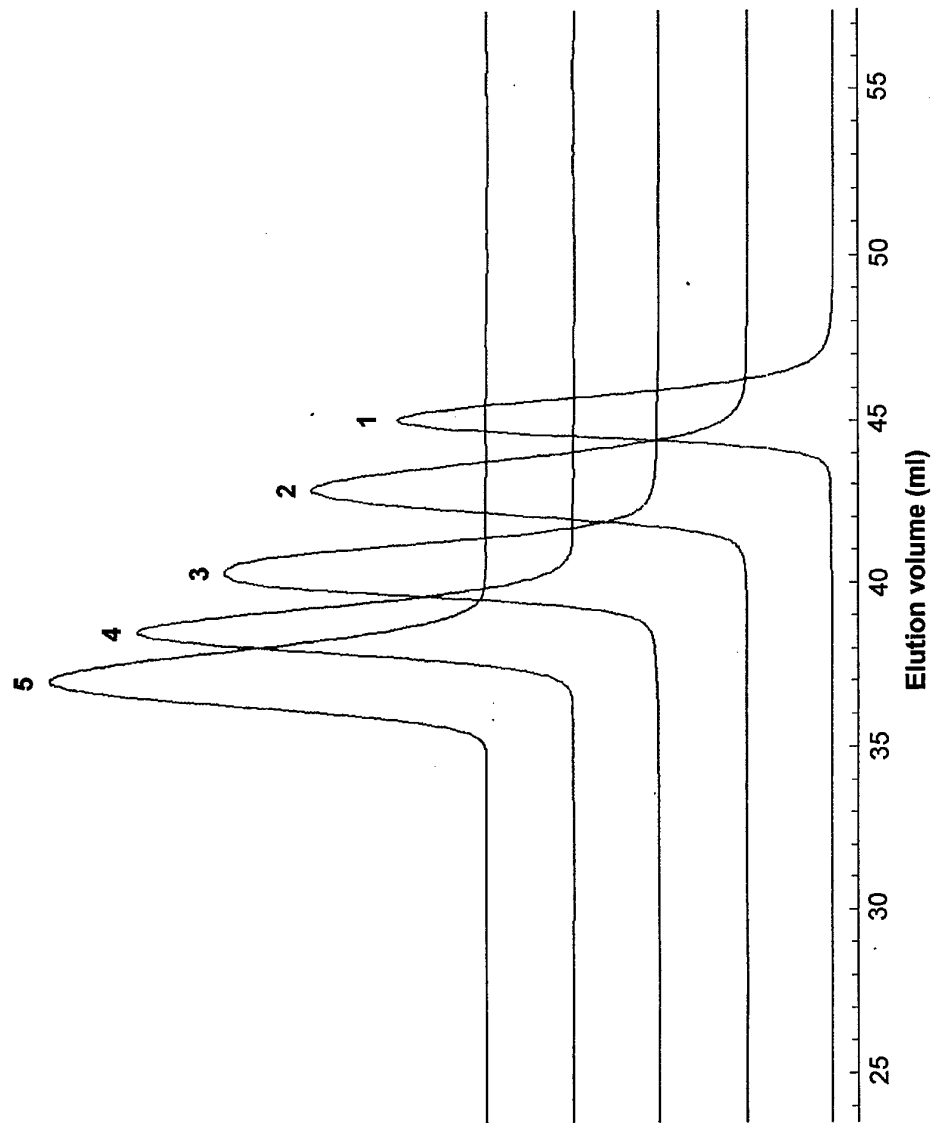
Elution volume (ml)

2) GPC traces of carbosilane dendrimers with the terminal cyanobiphenyl mesogenic groups: 1 - **G-1(Und-CB)$_8$**, 2 - **G-2(Und-CB)$_{16}$**, 3 - **G-3(Und-CB)$_{32}$**, 4 - **G-4(Und-CB)$_{64}$**, 5 - **G-5(Und-CB)$_{128}$** (10^3 Ultrastiragel 19×300 mm column, detector – UV spectrophotometer)
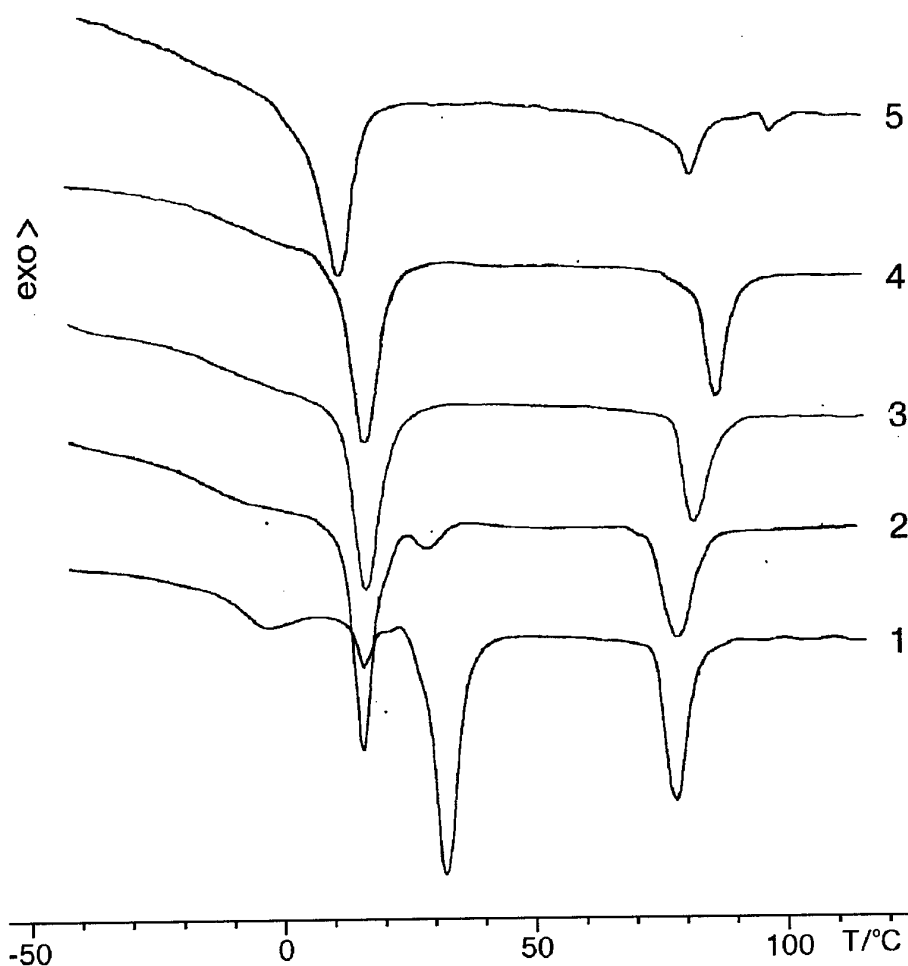
Attachment 3. Molecular mass parameters of the dendrimers synthesized calculated from the GPC data.

Dendrimer	MW_t	M_N (GPC)	M_W/M_N (GPC)	M_N(GPC)/ MW_t
G-1(All)$_8$	697	661	1.01	0.94
G-2(All)$_{16}$	1707	1360	1.01	0.80
G-3(All)$_{32}$	3728	2470	1.01	0.66
G-4(All)$_{64}$	7769	4170	1.01	0.54
G-5(All)$_{128}$	15850	6380	1.01	0.40
G-1(Und-CB)$_8$	4664	5710	1.01	1.22
G-2(Und-CB)$_{16}$	9640	9050	1.02	0.94
G-3(Und-CB)$_{32}$	19594	14500	1.02	0.74
G-4(Und-CB)$_{64}$	39501	20300	1.02	0.51
G-5(Und-CB)$_{128}$	79314	27200	1.02	0.34
G-1(Und-MPhB)$_8$	5052	5670	1.02	1.12
G-2(Und-MPhB)$_{16}$	10418	9440	1.02	0.91
G-3(Und-MPhB)$_{32}$	21148	14400	1.02	0.68
G-4(Und-MPhB)$_{64}$	42610	21100	1.02	0.49
G-5(Und-MPhB)$_{128}$	85532	24700	1.025	0.29
G-4(Pent-CB)$_{64}$	33225	17500	1.01	0.53

Note. MW_t - theoretical molar weight calculated from molar formula.

Attachment 4. DSC curves of some LC dendrimers investigated. (**3 pages**)

1) DSC traces of LC dendrimers *G-n(Und-MPhB)$_m$* : 1 - *G-1(Und-MPhB)$_8$* , 2 – *G-2(Und-MPhB)$_{16}$* , 3 - *G-3(Und-MPhB)$_{32}$* , 4 - *G-4(Und-MPhB)$_{64}$* , 5 - *G-5(Und-MPhB)$_{128}$*

2) Second heating (a) and first cooling (b) DSC traces of LC dendrimers *G-n(Und-CB)$_m$* : 1 - *G-1(Und-CB)$_8$* , 2 – *G-2(Und-CB)$_{16}$* , 3 - *G-3(Und-CB)$_{32}$* , 4 - *G-4(Und-CB)$_{64}$* , 5 - *G-5(Und-CB)$_{128}$*

3) DSC traces of LC dendrimers *G-n(Und-PBL)$_m$* : 1 - *G-1(Und-PBL)$_8$* , 2 – *G-2(Und-PBL)$_{16}$* , 3 - *G-3(Und-PBL)$_{32}$* .

1) DSC traces of LC dendrimers *G-n(Und-MPhB)$_m$* : 1 - *G-1(Und-MPhB)$_8$* , 2 – *G-2(Und-MPhB)$_{16}$* , 3 - *G-3(Und-MPhB)$_{32}$* , 4 - *G-4(Und-MPhB)$_{64}$* , 5 - *G-5(Und-MPhB)$_{128}$*

a)
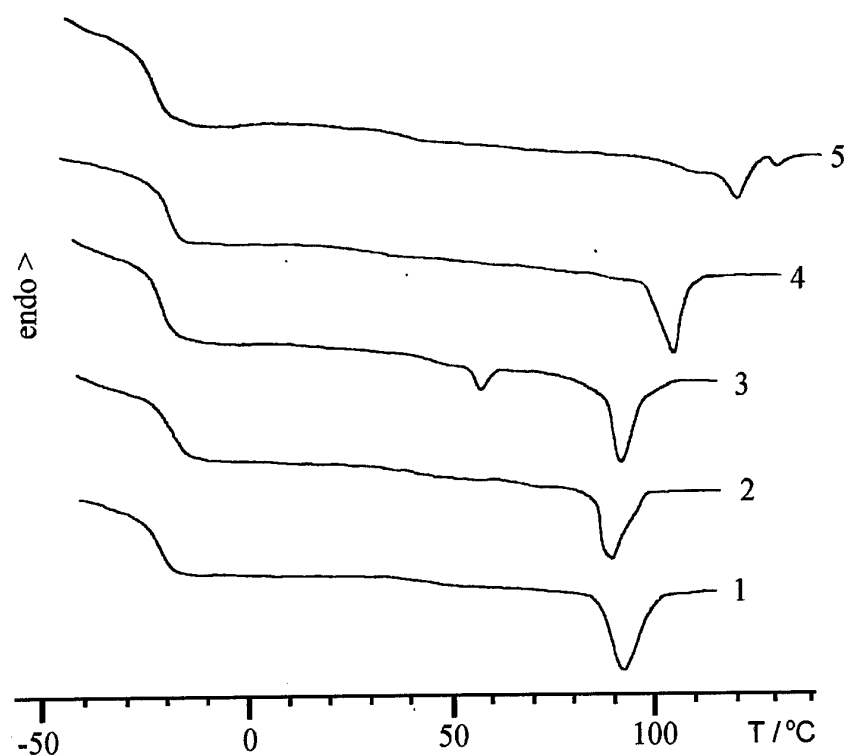
endo >

-50   0   50   100   T / °C

5

4

3

2

1

b)

< endo

150   100   50   0   T / °C

5

4

3

2

1

2) Second heating (a) and first cooling (b) DSC traces of LC dendrimers
$G\text{-}n(Und\text{-}CB)_m$: 1 - $G\text{-}1(Und\text{-}CB)_8$, 2 – $G\text{-}2(Und\text{-}CB)_{16}$,
3 - $G\text{-}3(Und\text{-}CB)_{32}$, 4 - $G\text{-}4(Und\text{-}CB)_{64}$, 5 - $G\text{-}5(Und\text{-}CB)_{128}$
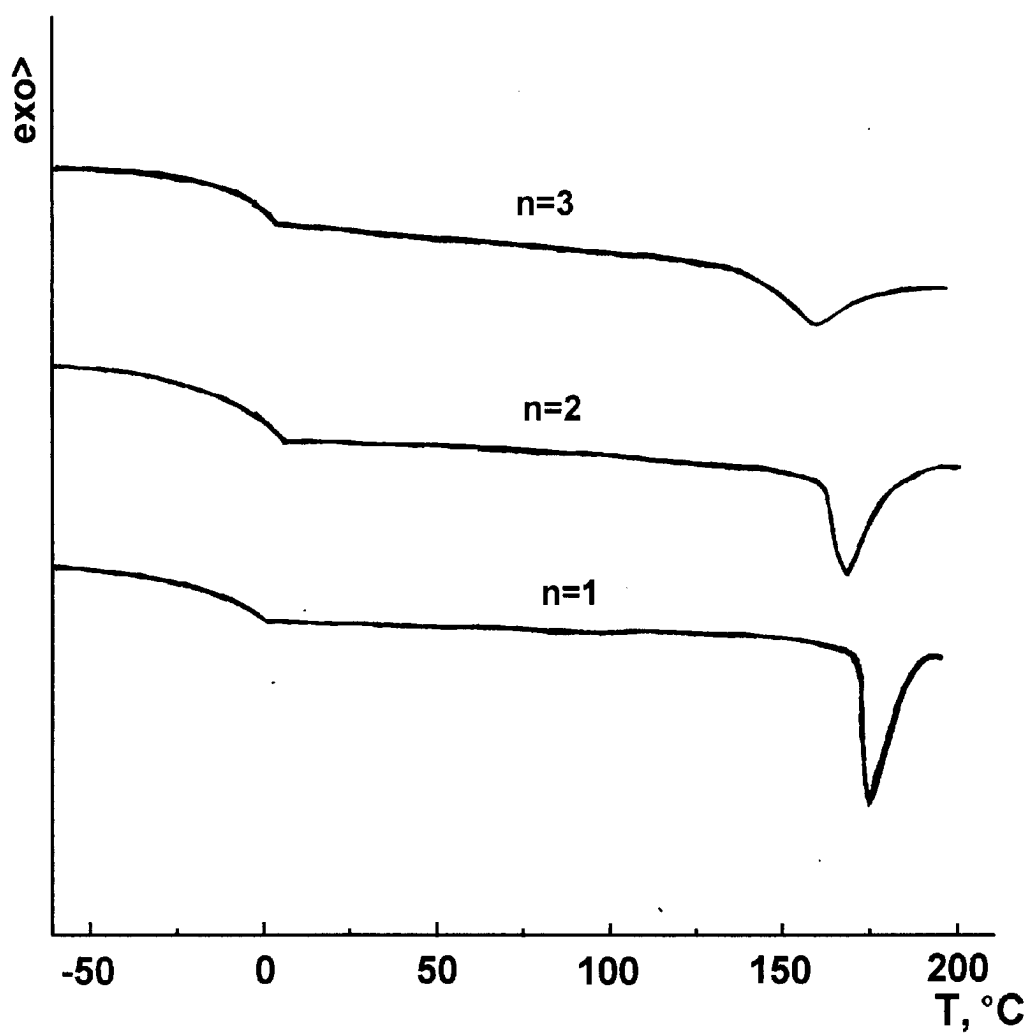
3) DSC traces of LC dendrimers $G-n(Und-PBL)_m$: 1 - $G-1(Und-PBL)_8$,
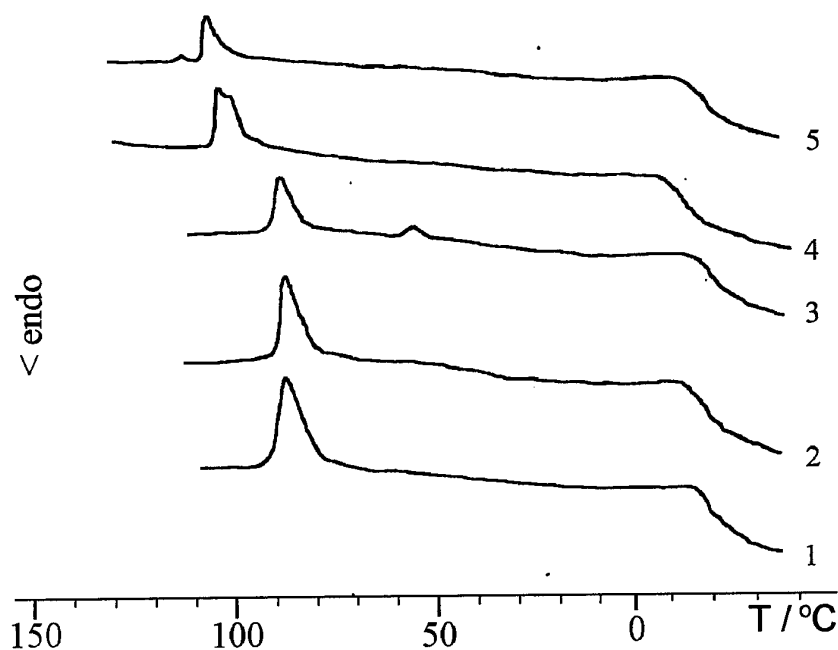   2 – $G-2(Und-PBL)_{16}$, 3 - $G-3(Und-PBL)_{32}$.

Attachment 5. Hydrodynamic and electrooptical properties of carbosilane LC dendrimers in toluene (tol) and chloroform (chl).

Sample	Molar mass	Sol-vent	T K	$[\eta]$ cm^3/g	$D\times10^{-7}$ cm^2/s	$A_o\times10^{10}$ $erg/Kmol^{-1/3}$	$K\times10^{10}$ SGSE units
G-1(Und-CB)₈	4656	tol	294	5.6	21	2.57	2.63
		tol.	329.6	4,4	-	-	-
G-2(Und-CB)₁₆	9640	tol	294	5.5	17	2.63	2.68
		tol	329.6	4.4	-	-	-
		chl	294	-	-	-	4.11
G-2(Und-MPhB)	10418	tol	294	5.7	16.7	2.68	-
		tol	329.6	4.8	-	-	-
		chl	285.9	7.2	-	-	-
		chl	294	6.5	-	-	-
G-3(Und-CB)₃₂	19594	tol	294	5.3	13.8	2.66	2.68
		tol	329.6	4.3	-	-	-
G-4(Und-CB)₆₄	39501	chl	294	6.2	-	-	4.32
G-4(Und-MPhB)	42610	tol	294	5.7	10	2.70	-
		tol	329.6	4.8	-	-	-
G-5(Und-CB)₁₂₈	79313	chl	285.9	7.5	-	-	-
		chl	310.9	6.3	-	-	-
		chl	294	-	-	-	4.21
		chl+tol	294	6.9	7.8	2.53	-

Note. T - temperature, $[\eta]$ - intrinsic viscosity, D - diffusion coefficient, A_o - hydrodynamic invariant, K - Kerr constant.